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FINAL REPORT

DEVELOPMENT OF HIGH ENERGY DENSITY
PRIMARY BATTERIES

BY

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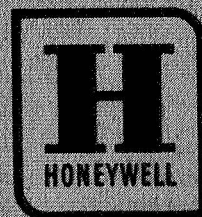
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PREPARED FOR

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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LIVINGSTON ELECTRONIC LABORATORY

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31 May 1967 to 30 April 1968

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S. G. ABENS, W. C. MERZ AND C. R. WALK

ABSTRACT

Experimental work for the development of CuF_2 -Li primary batteries was conducted. With methyl formate- LiAsF_6 electrolyte, 150 and 92 Wh/lb were obtained at 4.3 and 51 mA/cm², respectively. The lithium anodes were stable in this electrolyte. Purification of CuF_2 improved wet life, but depressed discharge potential of cells having propylene carbonate electrolyte. Purification of electrolyte did not improve CuF_2 electrode performance significantly.

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SUMMARY

This report describes experimental work for the development of CuF_2 -Li primary battery systems.

A. HIGH RATE BATTERY STUDY

A battery system using methyl formate (MF) as the electrolyte solvent was under study for the 1/2 to 30 hour discharge rate range. The solvent was Matheson, Coleman & Bell Spectroquality grade and was distilled from lithium powder for most tests.

1. Lithium Stability Tests: The compatibility of lithium in MF solutions of LiClO_4 , LiAsF_6 , LiSbF_6 , LiBF_4 , and LiPF_6 , and in some mixtures of these, was evaluated visually. A LiAsF_6 solution prepared metathetically from KAsF_6 and LiBF_4 appeared to be completely stable, while the other anions produced various degrees of discoloration of lithium or solution. With acetonitrile and dimethylformamide, LiAsF_6 did not produce stable solutions.
2. Solubility of CuF_2 and $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$: Solutions of LiClO_4 , LiAsF_6 , LiSbF_6 , and LiBF_4 were analyzed for Cu II content after 4 and 24 hours of agitation with CuF_2 or $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$. With CuF_2 , higher Cu II values (6g/L) were obtained in LiClO_4 and LiSbF_6 than in LiAsF_6 and LiBF_4 electrolytes (0.2 - 0.4g/L). About one order of magnitude higher solubility was obtained with $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ for all solutions.
3. Specific Conductance Measurements: When LiClO_4 was used as the solute, no synergistic effects were observed for mixtures of acetonitrile, dimethylformamide, and N-nitroso dimethylamine with MF. The highest conductivity measured was for 2M LiAsF_6 -MF electrolyte at 40 mmho/cm.
4. Cell Discharge Tests: In three-plate CuF_2 -Li cells, better performance was obtained with LiAsF_6 than with LiClO_4 or LiBF_4 electrolytes. The CuF_2 reduction efficiency obtained was 70 - 90% at 1 to 20 mA/cm². The optimum LiAsF_6 concentration was found to be 2 - 3 mols/liter, and 5 - 10 parts of $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ per 100 parts of CuF_2 produced the most desirable water content for the current density range of 1 to 40 mA/cm².

In 7-plate cell tests having about 5Ah of theoretical CuF_2 capacity and 9 sq. in. of cross-sectional positive electrode area (18 sq. in. working area), LiAsF_6 gave better results than LiClO_4 . Energy density of 150 wh/lb of net cell (electrodes, electrolyte, and separators) was obtained in 3M LiAsF_6 -MF electrolyte at -5°C and 4.3 mA/cm^2 . At 35°C , 138 wh/lb were obtained at 8.5 mA/cm^2 , and 137 wh/lb at 17 mA/cm^2 . At 51 mA/cm^2 , 92 wh/lb were obtained (ca. 1-hour rate).

B. LOW RATE BATTERY STUDY

Propylene carbonate (PC) was the electrolyte solvent of major interest for the development of a CuF_2 -Li battery for the 100 - 1000 hour discharge rate range.

1. Lithium Stability Tests: Visual tests of Li stability in solutions of various recrystallized and unrecrystallized salts were conducted. Recrystallization did not appear to improve stability in solutions made with purified PC. In 1M LiBF_4 solutions, better stability was indicated for PC than for trimethyl phosphate (TMP), glyme (G), or diglyme (DG).
2. CuF_2 Stability Tests: Recrystallization of electrolyte salts appeared to be effective for reduction of Cu II content in solution. For KAsF_6 , NaClO_4 , KSbF_6 , and NaPF_6 , the Cu II content was reduced from 100 - 300 ppm to below 60 ppm after 1000 hours of contact.

With 1M LiBF_4 solute, TMP produced much lower Cu II content than either PC, G, or DG (200 vs 2000 - 8000 ppm after 1000 hours).

Copper fluoride obtained from different manufacturers, as well as a lot purified by purging with gaseous F_2 , showed no significant difference in solubility after 1000 hours in 1M LiClO_4 -PC electrolyte. Extraction with DMSO prior to a 500-hour solubility test reduced the dissolved copper by one half (from ~ 500 to ~ 250 ppm).

Solubility of CuF_2 in tetraethylammonium fluoride (TEAF)-PC electrolyte was found to be very low (< 40 ppm). Lithium anodes were not visibly affected by this electrolyte, but they underwent severe polarization with even very small current drains. A similar result was obtained in TEAF-TMP electrolyte.

3. Cell Discharge Tests: Reducibility of CuF_2 in two plate test cells equipped with reference electrodes was studied. In electrolytes containing K or Na, reducibility was poor as compared with those containing Li cation. The effect of electrolyte purification and the use of various anions (AsF_6^- , BF_4^- , ClO_4^- , PF_6^-) was relatively insignificant.

In wet life tests with 3-plate cells, KAsF_6 -PC electrolyte gave the best performance (19% CuF_2 reduction after 2 weeks at 35°C). In LiBF_4 -PC electrolyte, cells having "high purity" grade or F_2 treated CuF_2 showed better wet life, but the discharge potential of these cells was depressed by as much as 1.0V.

1. INTRODUCTION

This report describes the results of experimental work performed under Contract NAS 3-10613 for NASA Lewis Research Center toward further development of high energy density primary batteries. The program was a continuation of work performed under Contract NAS 3-7632 (Final Report NASA CR-72331) and earlier contracts for the development of $\text{CuF}_2\text{-Li}$ battery systems.

In the present program, as in the previous one, two types of batteries for two distinct discharge rate ranges were considered. One was a battery for the 1/2 to 30-hour discharge rate range, for which methyl formate electrolyte with reserve activation appeared to be the best choice. The other was for the 100 to 1000 hour discharge time range, for which a non-reserve battery with propylene carbonate electrolyte appeared to be best suited.

For the high rate system, the major portion of the contractual effort was directed toward increasing both the discharge rate capability and the wet stand potential of the $\text{CuF}_2\text{-Li}$ system. For the low rate system, the major effort was directed toward finding methods for developing acceptable wet stand capability for the system.

2. HIGH RATE BATTERY STUDY

This section of the report discusses the development of a primary battery, capable of obtaining an energy density of over 50 wh/lb, for the 1/2 to 30-hour discharge rate range.

2. 1. Compatibility Tests

Methyl formate (MF) was the electrolyte solvent of primary interest for the high rate battery study, and most of the compatibility tests performed in this program involved the evaluation of various electrolyte salts in this solvent. The positive and negative electrode materials of primary interest were CuF_2 and Li, respectively, therefore, the stability of these materials in the various electrolytes was studied.

2. 1. 1. Preparation of Materials

A substantial portion of the contractual effort was expended in identification of possible harmful impurities and in devising methods for their removal. Where possible, routine analysis and purification of materials received from the vendors was practiced for the purpose of maintaining continuous control over the quality of the materials and the program.

2. 1. 1. 1. Purification of Methyl Formate

The methyl formate (MF) used in all tests was Matheson, Coleman and Bell's Spectroquality material. Purification consisted of agitating the solvent with powder lithium (1g Li/L of MF) and distilling it at room pressure thru a Vigreux column, collecting the middle 80% of the batch. Passing the solvent thru a Linde 4A Molecular Sieve prior to the Li powder treatment was added to the procedure after a high methanol content was reported for this material by another laboratory. A more detailed description of this method of methyl formate purification is given in Appendix A, page 92.

Other purification methods studied included extraction with aqueous NaCO_3 solution and distillation from P_2O_5 and SnCl_4 . The water content produced by these methods was about 50 - 100 ppm. Subsequent Li stability tests showed that these methods had no advantage over lithium powder drying.

2. 1. 1. 2. Purification of Electrolyte Salts

For all of the work in which LiClO_4 solute was used, the salt was purified by vacuum drying at elevated temperatures ($110 - 150^\circ\text{C}$), with Karl Fischer analysis being used for monitoring water content. The other salts studied in the program were vacuum dried only, except for KAsF_6 and KSbF_6 which were also purified by recrystallization from acetone as described in the next section. The water content of salts prepared by this procedure was in the range of 100 - 500 ppm.

2. 1. 1. 3. Metathetical Preparation of Electrolyte Solutions

Because the dry salts were either unavailable or of insufficient purity as received from the vendors, LiPF_6 , LiAsF_6 , and LiSbF_6 electrolytes were prepared by metathesis in solution from LiBF_4 and the potassium salt of the required anion. This method was found to be practical because of the relatively low solubility of KBF_4 in MF.

Since KAsF_6 and KSbF_6 were found to contain up to 10% acetone-insoluble impurities, these salts were recrystallized from methyl formate or acetone by adding dioxane to the concentrated solutions. The LiBF_4 as received was of high purity, and therefore was vacuum dried only. The solutions were prepared in methyl formate which was purified as described previously.

2. 1. 1. 4. Preparation of Dry LiAsF_6

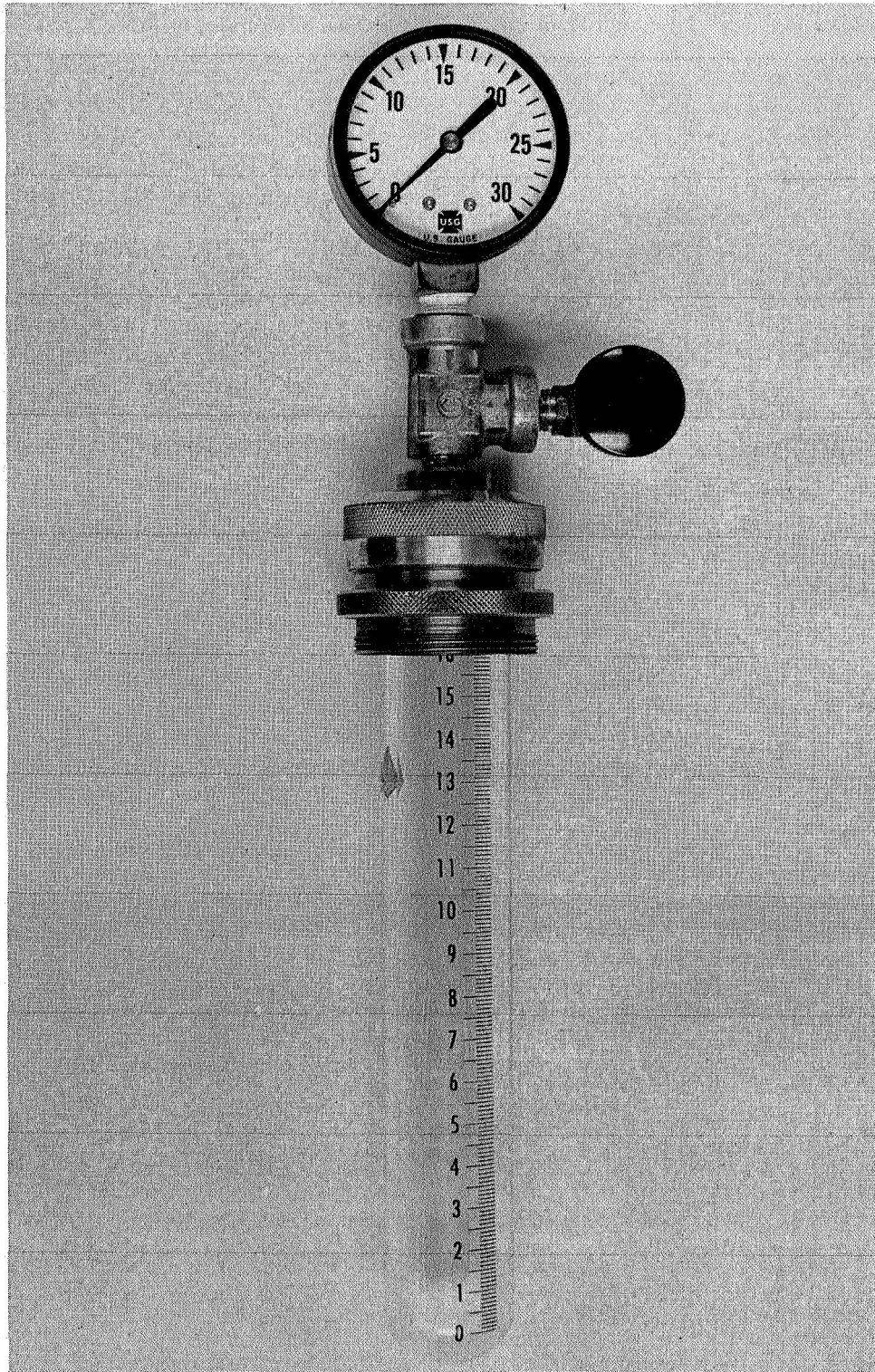
Some LiAsF_6 dry powder was also prepared in order to study its properties better. For this preparation, the metathesis was carried out in liquid ammonia, since unsolvated LiAsF_6 could not be recovered from methyl formate without decomposition of the materials. Using the NH_3 vehicle, however, a white, solvent-free product was obtained.

2. 1. 2. Lithium Stability in Electrolyte Solutions

Even in a short life battery, stability of the lithium in the electrolyte is of major interest, since decomposition products could form blocking films at the anode and cause cells to develop high operating pressures. The tests run in this part of the program were of short duration (24 hours), using visual appearance and pressure as stability criteria.

2. 1. 2. 1. Test Assembly

The tests were assembled by immersing a strip of $1/2 \times 1/16$ in. lithium, pressed onto expanded silver, in 5 - 10 ml of the test solution held in a 3 oz. glass compatibility tube. The tubes were equipped with pressure gauges and seals as seen in Figure 1, page 7.



TEST ASSEMBLY FOR LITHIUM STABILITY TESTS

FIGURE 1

2. 1. 2. 2. Tests With Various Solutes In Methyl Formate

Results of these tests are described in Table I, page 9, and photographs of selected test samples after 1, 24, and 52 hours of exposure are shown in Figures 2 - 4, pages 11 - 13.

The best stability, by both appearance and pressure criteria, was shown by LiAsF_6 electrolytes. These solutions also consistently showed a loss of the amber color upon contact with the lithium samples. The lithium showed a brownish film when placed in the electrolyte; however, this film did not form on a fresh Li piece when placed in the same solution after several days. This indicated that the color producing impurity had been reduced, and that lithium can be used to purify this electrolyte.

The addition of 10 mol percent of LiAsF_6 to other electrolytes improved their stability to some extent. However, discoloration was still more pronounced than with LiAsF_6 alone.

2. 1. 2. 3. Tests With LiAsF_6 In Dimethylformamide and Acetonitrile

Because of the good lithium stability shown by LiAsF_6 -MF solutions, compatibility of molar solutions of this salt in the above solvents (which are not compatible with Li in LiClO_4 solutions) were tested.

Both of the solutions tested produced considerable activity with the lithium test strip. The stabilization effect obtained with LiAsF_6 in MF was not observed with these solvents.

2. 1. 3. Solubility of CuF_2 and $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ In Various Electrolytes

Since the solubility of the cathode active material in the electrolyte is a measure of both the wet shelf life and discharge potentials of the battery, a number of solubility measurements were obtained. Both CuF_2 and $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ were studied in these tests to further identify the role of the dihydrate on the discharge performance of the CuF_2 electrodes.

Electrolyte and cathode materials were introduced into a 60 ml serum bottle. The bottles were agitated, samples were withdrawn and centrifuged, and Cu II contents were determined iodometrically.

Four electrolyte salts were compared in this test as shown in Table II, page 14. With CuF_2 (anhydrous), much higher solubility was obtained in

TABLE I
LITHIUM STABILITY TESTS IN MF ELECTROLYTES

<u>Solution</u>	<u>H₂O, ppm</u>	<u>Appearance*</u>	<u>Pressure, 48 Hrs. (psig)</u>
MF ¹	55	C	7.8
MF ²	65	C	(Leak)
MF ³	70	C	9.8
MF ⁴	70 ⁶	C	5.9
MF ⁵	200	C	9.2
4M LiClO ₄	140	B	9.0
4M LiBF ₄	350	C	8.0
4M LiAsF ₆	625	C	3.1
4M LiSbF ₆	400	C	4.4
3M LiAsF ₆	900	A	5.0
3M LiAsF ₆	358	A	1.0
3M LiAsF ₆	170	B	3.0
3M LiAsF ₆	170	B	4.0
3M LiClO ₄	140	B	5.0
3M LiClO ₄	140	B	15.0
3M LiClO ₄	88	C	7.1
3M LiPF ₆	140	C	5.0
2.7M LiClO ₄ } .3M LiAsF ₆ }	115	C	10.2
2.7M LiClO ₄ } .3M LiAsF ₆ }	143	B	6.0

¹Li powder

²SnCl₄

³13-X Sieve

⁴P₂O₅ + 5% BF₃ (MF distilled from P₂O₅ atmospheric pressure).

⁵As Received MF

⁶Water content of MF only, before addition of 5% BF₃

* "A" - No reaction after 24 hours - acceptable

"B" - No reaction after 2 hours - reaction after 24 hours; possibly acceptable

"C" - Reaction before 2 hours; not acceptable

TABLE I (Continued)
LITHIUM STABILITY TESTS IN MF ELECTROLYTES

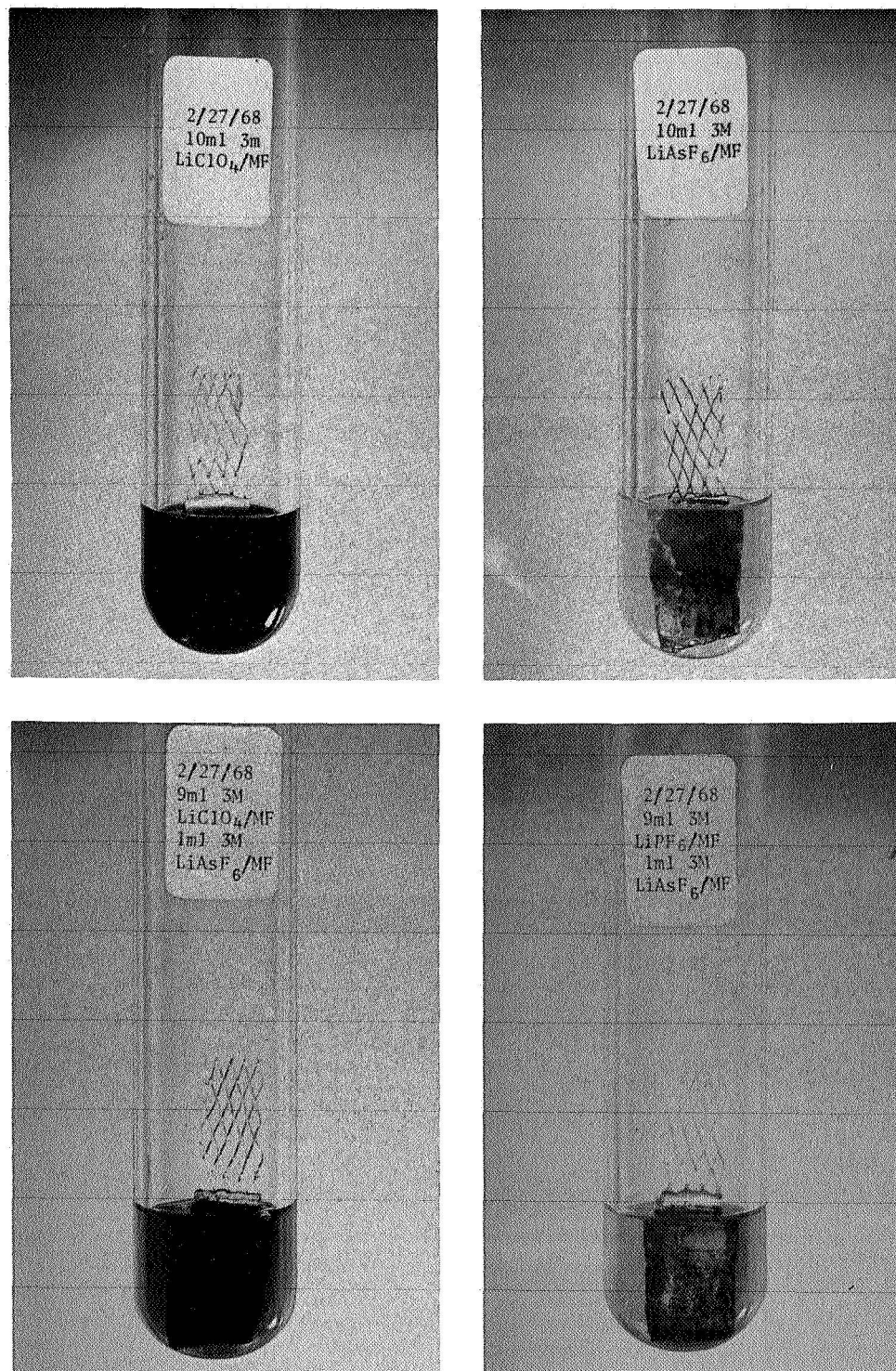
<u>Solution</u>	<u>H₂O, ppm</u>	<u>Appearance*</u>	<u>Pressure, 48 Hrs. (psig)</u>
2.7M LiClO ₄ } .3M LiAsF ₆ }	143	B	10.0
2.7M LiClO ₄ } .3M LiBF ₄ }	101	C	8.2
2.7M LiPF ₆ } .3M LiBF ₄ }	160	C	3.0
2.7M LiPF ₆ } .3M LiAsF ₆ }	160	C	5.0
2.7M LiPF ₆ } .3M LiAsF ₆ }	143	B	6.0
2.7M LiBF ₄ } .3M LiAsF ₆ }	332	B	8.0

* "A" - No reaction after 24 hours - acceptable

"B" - No reaction after 2 hours - reaction after 24 hours; possibly acceptable

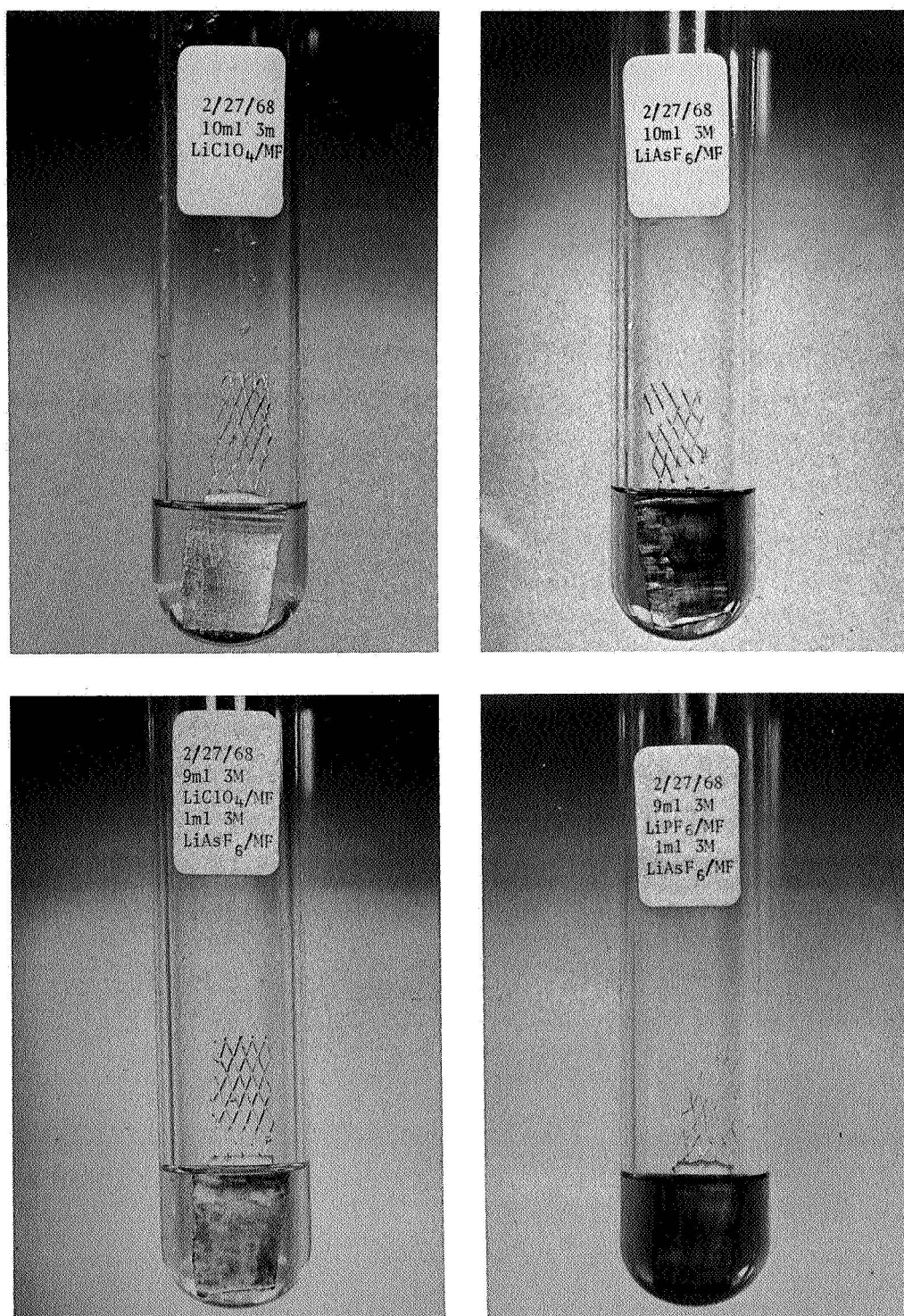
"C" - Reaction before 2 hours; not acceptable

LiClO₄ and LiSbF₆ (6.2g Cu/L) than in LiBF₄ (0.4g/L) and LiAsF₆ (0.2g/L) electrolytes. As expected, much higher solubility was obtained with CuF₂·2H₂O in all electrolytes, and there was less difference between the values for the different solutes (solubility range was 9 to 18g Cu/L).



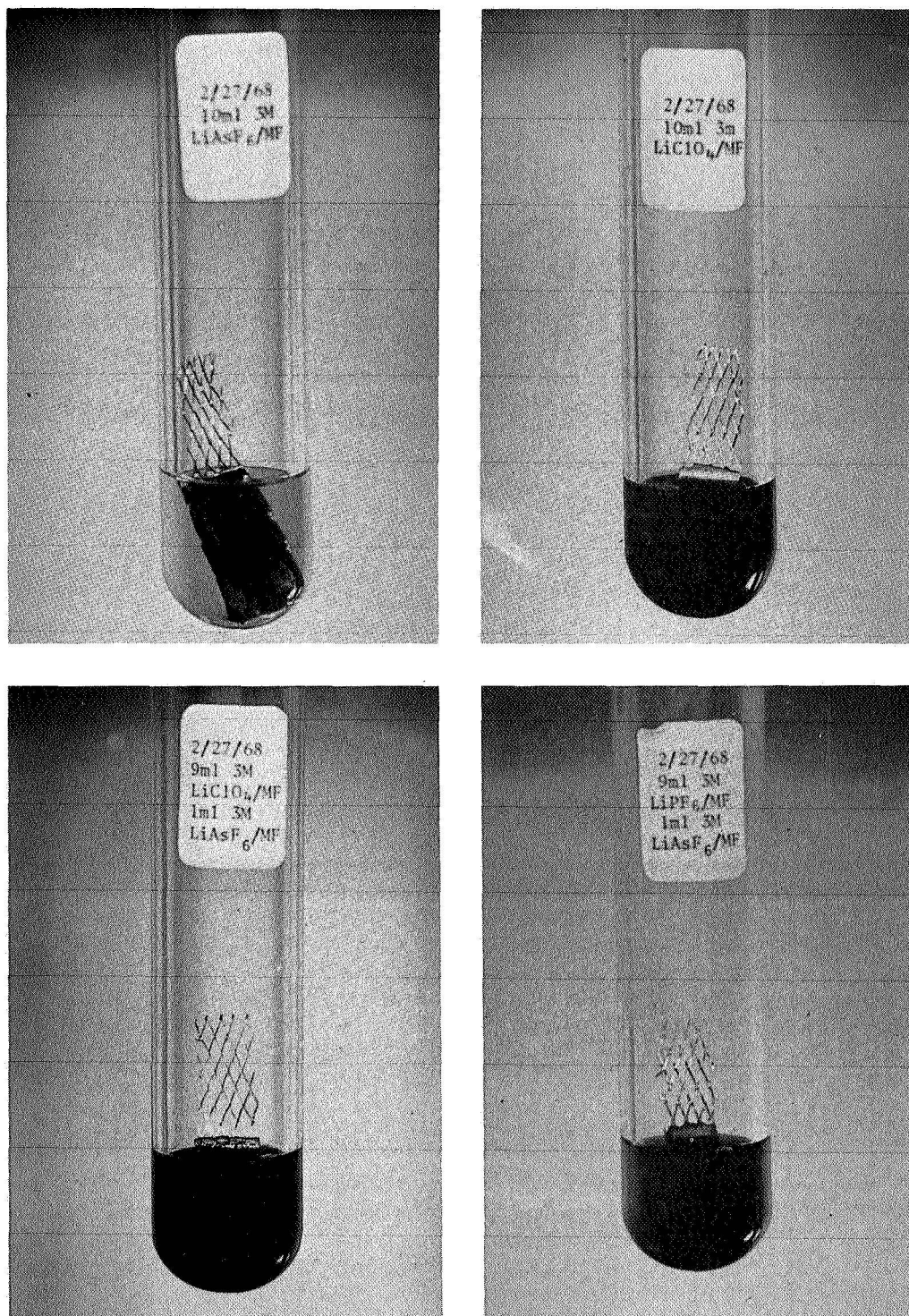
STABILITY OF Li IN METHYL FORMATE ELECTROLYTES
AT ONE HOUR

FIGURE 2



STABILITY OF Li IN METHYL FORMATE ELECTROLYTES
AT 24 HOURS

FIGURE 3



STABILITY OF Li IN METHYL FORMATE ELECTROLYTES
AT 52 HOURS

FIGURE 4

TABLE II
SOLUBILITY OF CuF_2 AND $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ IN 3M MF ELECTROLYTES

<u>Electrolyte</u>	<u>Water, ppm</u>	<u>Cu ⁺⁺ Concentration, μg/ml</u>	
		<u>4 Hours</u>	<u>24 Hours</u>
<u>A. 1.0g CuF₂/20 ml Electrolyte</u>			
LiClO ₄	140	600	6,200
LiAsF ₆	170	200	200
LiBF ₄	350	205	395
LiSbF ₆	440	2,460	6,150
2.7M LiClO ₄ } 0.3M LiAsF ₆	143	500	2,600
2.7M LiBF ₄ } 0.3M LiAsF ₆	332	100	200
<u>B. 1.4g CuF₂·2H₂O/20 ml Electrolyte</u>			
LiClO ₄	140	7,600	10,800
LiAsF ₆	170	8,500	9,200
LiBF ₄ *	350	8,100	11,685
LiSbF ₆ *	440	6,960	18,145
2.7M LiClO ₄ } 0.3M LiAsF ₆	143	14,700	18,500
2.7M LiBF ₄ } 0.3M LiAsF ₆	332	8,500	7,800

*1.0g $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ /20 ml Electrolyte

2. 2. Electrolyte Conductivity Measurements

Conductivity values were obtained for a number of candidate electrolytes as well as for some other methyl formate solutions. Measurements were made at 1000 Hz using a smooth platinum electrode cell with a constant of about 1.0.

2. 2. 1. Effect of Electrolyte Concentration in Methyl Formate

Conductivity measurements of LiBF_4 , LiAsF_6 , and LiSbF_6 solutions (with LiClO_4 included for comparison), over the concentration range of one molar to saturated, were obtained. At room temperature (27°C), the saturation concentration for the three salts appeared to be between 3 and 4 molar; however, since the organic solutions come to equilibrium very slowly, accurate saturation points cannot be quickly obtained.

The conductivities of 2M solutions of LiAsF_6 (40.2 mmho/cm) and LiSbF_6 (39.1 mmho/cm) were the highest. Values obtained for the other concentrations and salts are shown in Table III.

TABLE III

SPECIFIC CONDUCTANCE OF METHYL FORMATE SOLUTIONS

Temperature: $27^\circ \pm 1^\circ\text{C}$

<u>Salt</u>	<u>Specific Conductance, mmho/cm</u>			
	<u>4M</u>	<u>3M</u>	<u>2M</u>	<u>1M</u>
LiClO_4	23.6	29.7	28.5	15.7
LiBF_4	17.4*	18.3	14.3	7.3
LiAsF_6	29.5*	33.5	40.2	29.7
LiSbF_6	24.0*	25.9	39.1	35.6

*Saturated

2. 2. 2. Conductivity of LiClO_4 in Mixed Solvents

The possibility of enhancing electrolyte conductivity by adding a second solvent to methyl formate was studied. For this test, dimethylformamide (DMF), N-nitroso dimethylamine (NDA), and acetonitrile (AN) were selected, mainly because of their high dielectric constants.

Results of the conductivity measurements are shown in Table IV, page 16. No synergistic effect was found with any of the solvents studied, and this approach for improving conductivity was not pursued further in this contract.

TABLE IV
SPECIFIC CONDUCTANCE OF LiClO_4 IN MIXED SOLVENTS

LiClO_4 Conc., g/100 ml	mmho/cm				
	100% MF	25% DMF	50% DMF	75% DMF	100% DMF
25	25.4	17.8	16.4	13.9	10.8
50	23.4	16.5	9.9	5.8	1.7
	100% MF	25% NDA	50% NDA	75% NDA	100% NDA
25	25.4	20.0	16.4	12.2	8.5
50	23.4	15.7	9.6	5.0	1.7
	100% MF	25% AN	50% AN	75% AN	100% AN
25	25.4	25.0	25.6	26.3	31.3*

*Saturated solution

2. 2. 3. Conductivity of LiAsF_6 in Dimethylformamide and Acetonitrile

In order to study the behavior of LiAsF_6 in other candidate high rate solvents, sufficient salt was dissolved in both dimethylformamide and acetonitrile to produce 3M solutions. The 3M LiAsF_6 :DMF solution appeared to be unsaturated. The LiAsF_6 dissolved completely in the AN, but a quantity reprecipitated within one hour. When the solution was diluted to 2M, the salt dissolved; but upon standing overnight, a quantity of it reprecipitated. The specific conductance of the supernatant liquid was 43.6 mmho/cm, while that of the 3M LiAsF_6 :DMF was 17.8 mmho/cm.

2. 2. 4. Other Conductivity Measurements in MF

Conductivities of a number of other MF solutions were obtained in the program. Although these solutions were not considered to be candidate electrolytes for the high rate battery (most were solutions for metathetical preparation of their lithium counterparts), the values may be of interest and are given in Table V, page 17.

TABLE V
SPECIFIC CONDUCTANCE OF VARIOUS SOLUTES IN MF

	<u>L_s, mmho/cm</u>			
	<u>1.00 M</u>	<u>1.25 M</u>	<u>2.5 M</u>	<u>5.0 M</u>
NaClO_4	13	--	21	24*
KAsF_6	19	--	25	27*
KPF_6	10	--	11*	11*
KSbF_6	26	29	32	32*
NaAsF_6	--	26	--	25*

*Saturated solutions

2. 3. Cell Discharge Tests

About 150 3-plate and 70 7-plate cells were built and discharged in the high rate battery development effort. The purpose of this work was to evaluate physical and chemical construction variables, and to characterize the MF battery system further.

2. 3. 1. Preparation of Electrodes

All cells constructed in this part of the program had thin plate electrodes measuring about 2 x 1.5 in. Commercial lithium (about 99.99% purity) was used for the negative electrodes, and 99.5% purity CuF_2 and $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ were used in the positive ones. The purity level of these materials was monitored by X-ray diffraction analysis.

2. 3. 1. 1. Pasted CuF_2 Plates

Two types of pasted positive plates, differing in binder and pasting solvent, were used in the program. Paste compositions using cellulose acetate binder and a 90% ethyl acetate-10% ethanol pasting solvent were developed in the previous contract, and were used in this program for only one test (evaluation of 7-plate cell performance with LiClO_4 electrolyte). All other tests in this program used pastes having a polystyrene binder and xylene pasting solvent. This binder-solvent combination was adopted mainly because it is non-hygroscopic, which allows some

handling at room atmosphere without contamination with moisture. Performance of plates with polystyrene binder was found to be equal to that of plates with cellulose acetate binder.

The pastes were made by mixing the CuF_2 and $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ with the conductor (carbon black or graphite) in a Hi-Speed Micronizer-Blender for 20 seconds to 1 minute, then adding enough of the pasting vehicle to give a workable paste consistency. The paste was applied to expanded silver grids in a polypropylene pasting cavity. The solvent was removed and the plates were stored under hard vacuum until they were used for building cells.

2. 3. 1. 2. Pressed Lithium Plates

The negative electrodes were prepared by placing lithium sheet (0.015 in. thick) and expanded metal between polyethylene sheets and pressing to just below the pressure at which lithium begins to flow (ca. 1000 psi). The electrodes were stored under hard vacuum for no more than 24 hours before construction of cells.

2. 3. 2. Performance of Three-Plate (Positive Limited) Cells

In order to study positive electrode performance, cells were built with one positive and two negative electrodes, the latter having a large over-capacity to assure positive limitation in discharge. The separation employed was 0.02 in. glass filter mat, and heat sealed polyethylene envelopes served as cases. At the lower test temperature (-5°C), the cells were racked for discharge, while at 35°C , the tests were performed in hermetically sealed polyethylene test fixtures (see Figure 20, page 42).

2. 3. 2. 1. Electrolyte Salt Studies

A series of discharge tests were performed to compare cathode performance in cells using LiClO_4 , LiBF_4 , and LiAsF_6 (LiSbF_6 was dropped from consideration because of the apparent instability of the hexafluoroantimonate ion with lithium metal in MF). The positive paste composition was: CuF_2 - 100; $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ - 10; Conductex SC - 10; polystyrene (5% solution in Xylene) - 1. The cells were discharged at 1, 8.3, and 20 mA/cm^2 after a wet stand of 30 minutes at -5°C , giving the results shown in Table VI, page 19. The voltage-time curves for the best discharge at each current are also plotted in Figures 5 - 7, pages 20 - 22.

The data presented indicate that a considerable improvement in cell performance results from substituting LiAsF_6 for LiClO_4 (the previously favored electrolyte salt) or LiBF_4 in MF. This improvement becomes even more definite at low current densities (1 mA/cm^2), where the demonstrated

TABLE VI
PERFORMANCE OF CuF_2 -Li CELLS WITH 3M METHYL FORMATE ELECTROLYTES AT -5°C

Cell No.	Cathode Thickness, inches	Cathode Theo. Capacity, AH	Solute	Current Density mA/cm ²	Time to VF, Hrs.	Cathode Eff., %
1	0.045	1.37	LiClO_4	1.0	9.00*	26
2	0.043	1.34	"	"	9.16*	28
3	0.046	1.39	LiBF_4	"	12.25*	35
4	0.041	1.34	"	"	12.33*	37
5	0.048	1.25	LiAsF_6	"	22.33*	71
6	0.041	1.29	"	"	17.00*	53
7	0.046	1.39	LiClO_4	8.3	2.83**	68
8	0.050	1.59	"	"	3.42**	72
9	0.044	1.36	LiBF_4	"	2.00**	49
10	0.045	1.23	"	"	1.67**	45
11	0.047	1.46	LiAsF_6	"	3.50**	80
12	0.041	1.27	"	"	2.80**	73
13	0.043	1.28	LiClO_4	20.0	1.08**	67
14	0.043	1.34	"	"	1.17**	70
15	0.038	1.28	LiBF_4	"	0**	--
16	0.045	1.41	"	"	0**	--
17	0.042	1.35	LiAsF_6	"	1.50**	89
18	0.040	1.31	"	"	1.27**	78

*2.5VF

**2.0VF

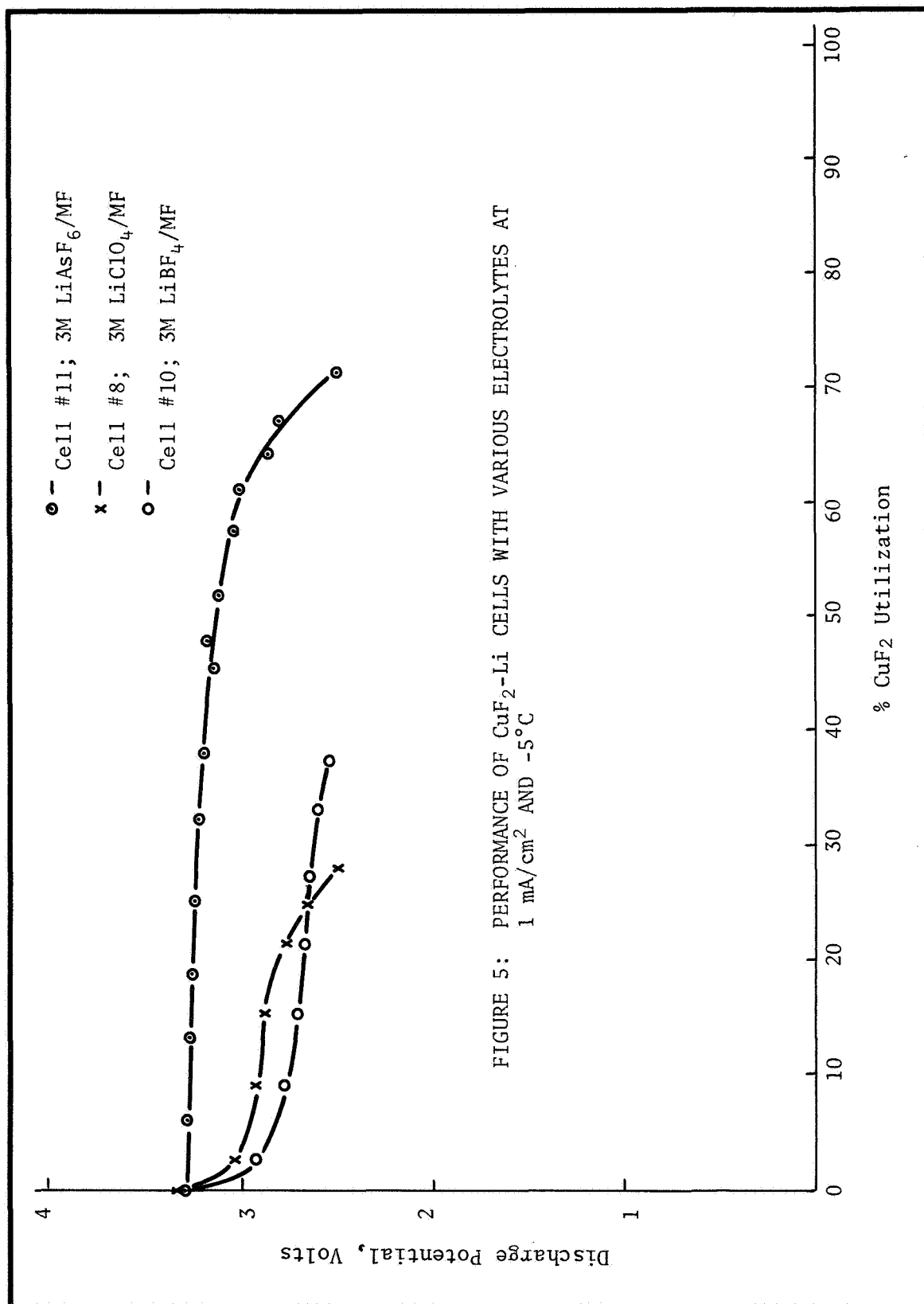


FIGURE 5

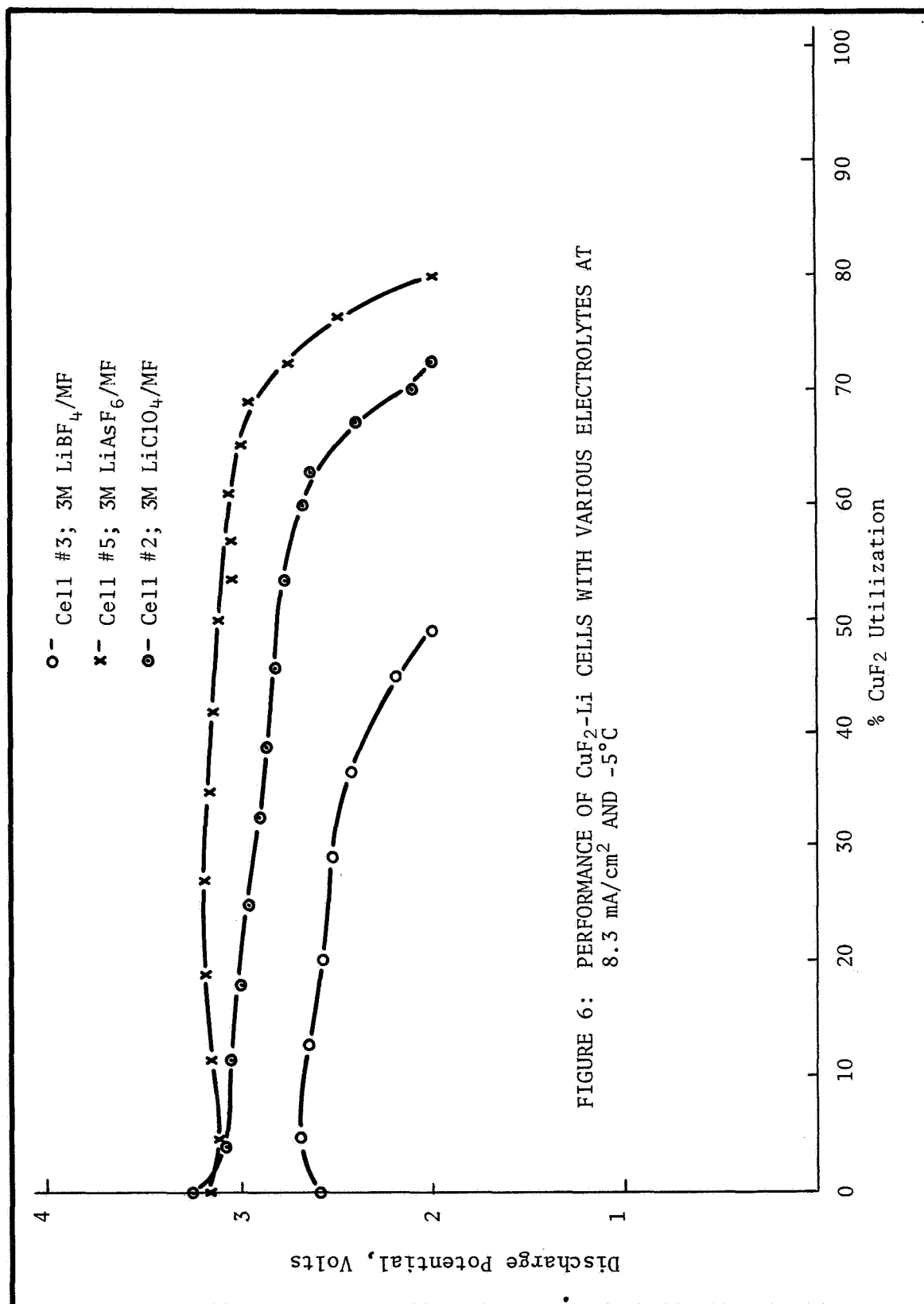


FIGURE 6: PERFORMANCE OF CuF₂-Li CELLS WITH VARIOUS ELECTROLYTES AT 8.3 mA/cm² AND -5°C

FIGURE 6

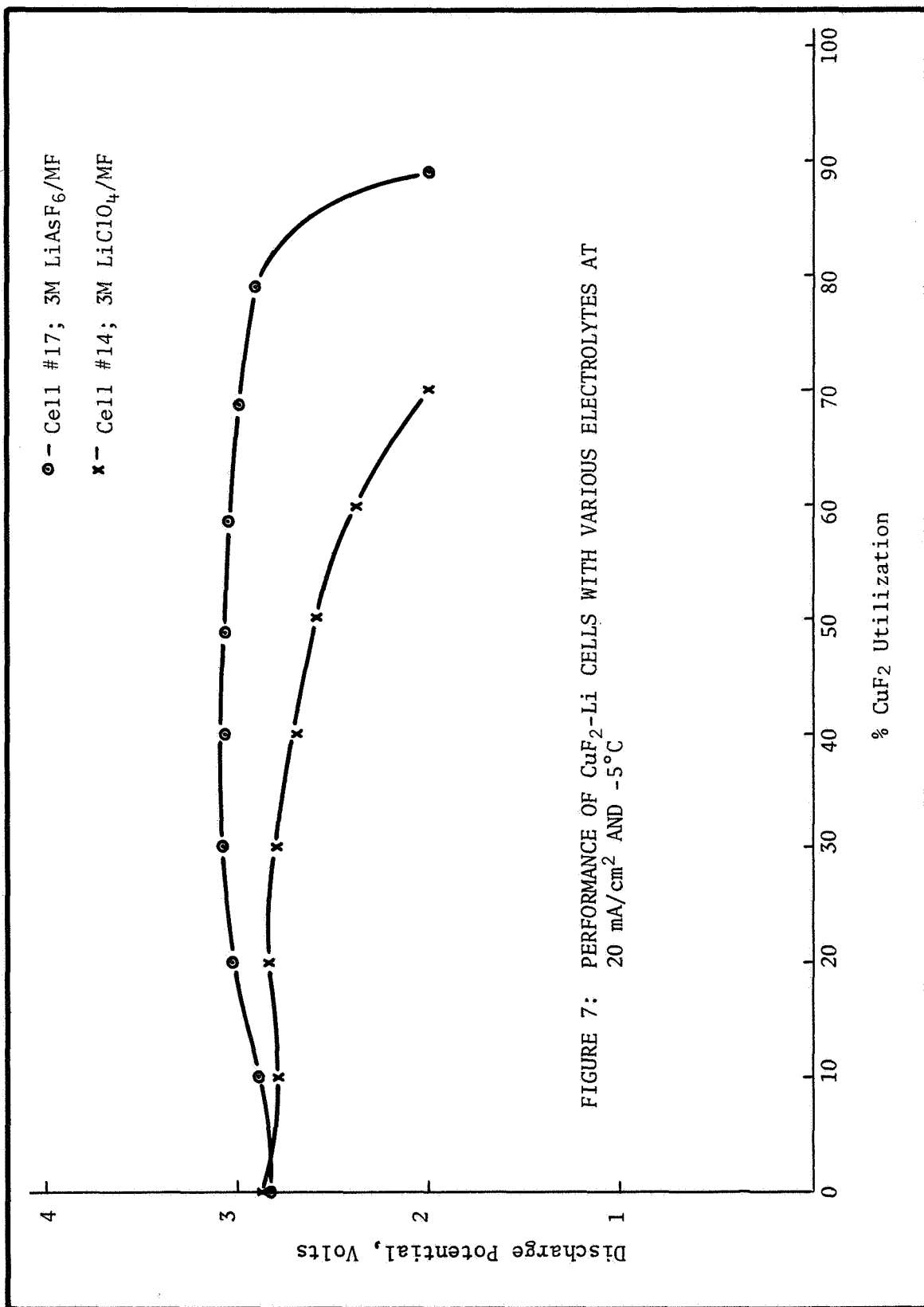


FIGURE 7

superior lithium stability of LiAsF_6 allows longer discharge times at higher average potentials. At higher current densities, the higher conductivity of the LiAsF_6 electrolyte probably accounts for the better discharge performance.

2. 3. 2. 2. Solute Concentration Studies

Three-plate cells were assembled and tested to determine the optimum LiAsF_6 concentration over a range of discharge rates. The positive electrode compositions were the same as described in the previous section, except that 5 parts of $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ were used to 100 parts of CuF_2 . Construction and discharge data for these cells are shown in Table VII, page 24.

Cells containing 2 and 3 molar electrolytes gave the best performance. At the lowest current density (1 mA/cm^2), 3 molar was better; at the higher current densities, variation in performance between the two concentrations appeared to be within experimental error for the test. At a current density of 20 mA/cm^2 , cathode utilization efficiencies of 80% were recorded for cells containing both 2 and 3 molar electrolytes.

2. 3. 2. 3. Effect of Dihydrate Content

The relatively high discharge rates (up to 40 mA/cm^2) for the CuF_2 -Li couple in MF electrolytes can only be obtained if sufficient water is present in the cathode to solubilize the CuF_2 ¹. The optimum water content of the electrode probably varies with the discharge rate and operating temperature. In this test, the current density range of 1 to 40 mA/cm^2 was employed (ca. 20 to 1/2-hour rate, respectively) to evaluate the effect of several $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ levels on cell performance in LiAsF_6 -MF electrolyte.

Construction and discharge data are shown in Table VIII, page 25, and V-T curves for selected cells are plotted in Figures 8 and 9, pages 26 and 27. Five grams of dihydrate/100g CuF_2 appeared to give adequate water for the higher discharge currents (the somewhat higher efficiencies obtained with this mixture at 30 and 40 mA/cm^2 compared to the 10g $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ /100g CuF_2 mixture are within experimental error limits).

¹See, for example, NASA CR-72331, pp. 104 - 107.

TABLE VII
EFFECT OF LiAsF_6 CONCENTRATION ON PERFORMANCE OF CuF_2 -Li CELLS AT -5°C

Cell No.	Electrolyte Concentration, Mols/L	Theo. CuF_2 Cap., AH	Load	Final Volts	Average Discharge Potential, Volts	Time to VF, Hrs.	Cap. to VF, AH	% CuF_2 Utilized
1	1	1.48	.04A	2.50	3.00	3.08	.32	21.6
2	1	1.49	"	2.50	3.05	10.50	.42	28.2
3	2	1.48	"	2.50	3.09	14.00	.56	37.8
4	2	1.49	"	2.50	3.09	11.33	.45	30.2
5	3	1.50	"	2.60	3.05	24.50	.95	65.4
6	3	1.49	"	2.50	3.03	20.25	.81	54.3
7	Saturated*	1.57	"	2.50	2.97	13.50	.54	34.4
8	Saturated*	1.62	"	2.50	2.99	19.42	.78	48.1
9	1	1.39	.24A	2.00	2.59	2.50	.60	43.2
10	1	1.42	"	2.00	2.72	3.18	.76	53.6
11	2	1.59	"	2.00	2.88	5.33	1.28	80.5
12	2	1.46	"	2.00	2.70	3.85	.95	63.6
13	3	1.52	"	2.00	2.57	4.83	1.16	76.4
14	3	1.45	"	2.00	2.58	4.10	.98	67.6
15	Saturated*	1.28	"	2.00	2.63	4.50	1.08	84.4
16	Saturated*	1.51	"	2.00**	2.32	4.85	1.16	76.9
17	1	1.38	.80A	2.00	2.30	.75	.60	43.4
18	1	1.49	"	2.00	2.09	.49	.37	26.2
19	2	1.41	"	2.00	2.48	1.27	1.02	72.1
20	2	1.51	"	2.00	2.64	1.52	1.22	80.9
21	3	1.30	"	2.00	2.51	1.30	1.04	80.0
22	3	1.44	"	2.00	2.25	1.17	.94	65.3
23	Saturated*	1.36	"	1.50**	1.64	1.35	1.08	79.4
24	Saturated*	1.48	"	1.50**	1.54	1.42	1.13	76.7

* Less than 4 mols/L.

**Voltage dropped below 2.00V during discharge.

TABLE VIII
COMPOSITION OF CuF₂-Li CELLS AND DISCHARGE PERFORMANCE IN 3M LiAsF₆/MF

Cell No.	g CuF ₂ •2H ₂ O/ 100g CuF ₂ *	Theo. CuF ₂ Cap., AH	Electrolyte Volume, cc	Dischg. Temp., °C	Discharge Current, A	Discharge Current Density, mA/cm ²	Time to 2.0 VF, Hours	Average E to 2.0VF, Volts	% CuF ₂ Reduced
1	10	1.41	5	- 5	0.040	1.0	21.12	3.06	60.3
2	10	1.48	5	- 5	"	"	19.30	3.08	52.2
3	5	1.35	5	- 5	"	"	22.50	3.04	66.5
4	5	1.30	5	- 5	"	"	20.75	3.07	63.8
5	1	1.26	5	- 5	"	"	11.83	2.79	37.4
6	1	1.41	5	- 5	"	"	18.50	3.02	52.5
7	10	1.31	7	- 5	0.240	6.0	4.50	2.95	82.5
8	10	1.58	7	+35	"	"	4.17	2.96	63.3
9	5	1.25	7	- 5	"	"	3.83	2.90	73.7
10	5	1.38	7	+35	"	"	3.97	3.01	68.9
11	1	1.31	7	- 5	"	"	2.83	2.78	51.8
12	1	1.34	7	+35	"	"	4.25	3.04	76.2
13	10	1.53	7	+35	1.20	30.0	1.00	2.56	78.4
14	10	1.46	7	- 5	0.80	20.0	.93	2.32	50.9
15	5	1.48	7	+35	1.20	30.0	1.00	2.59	81.1
16	5	1.39	7	- 5	0.80	20.0	1.08	2.39	62.1
17	10	1.36	7	+35	1.60	40.0	0.45	2.37	52.9
18	5	1.31	7	+35	1.60	40.0	0.53	2.45	64.9

*10g Conductex SC and 1g polystyrene/100g CuF₂ in all cells

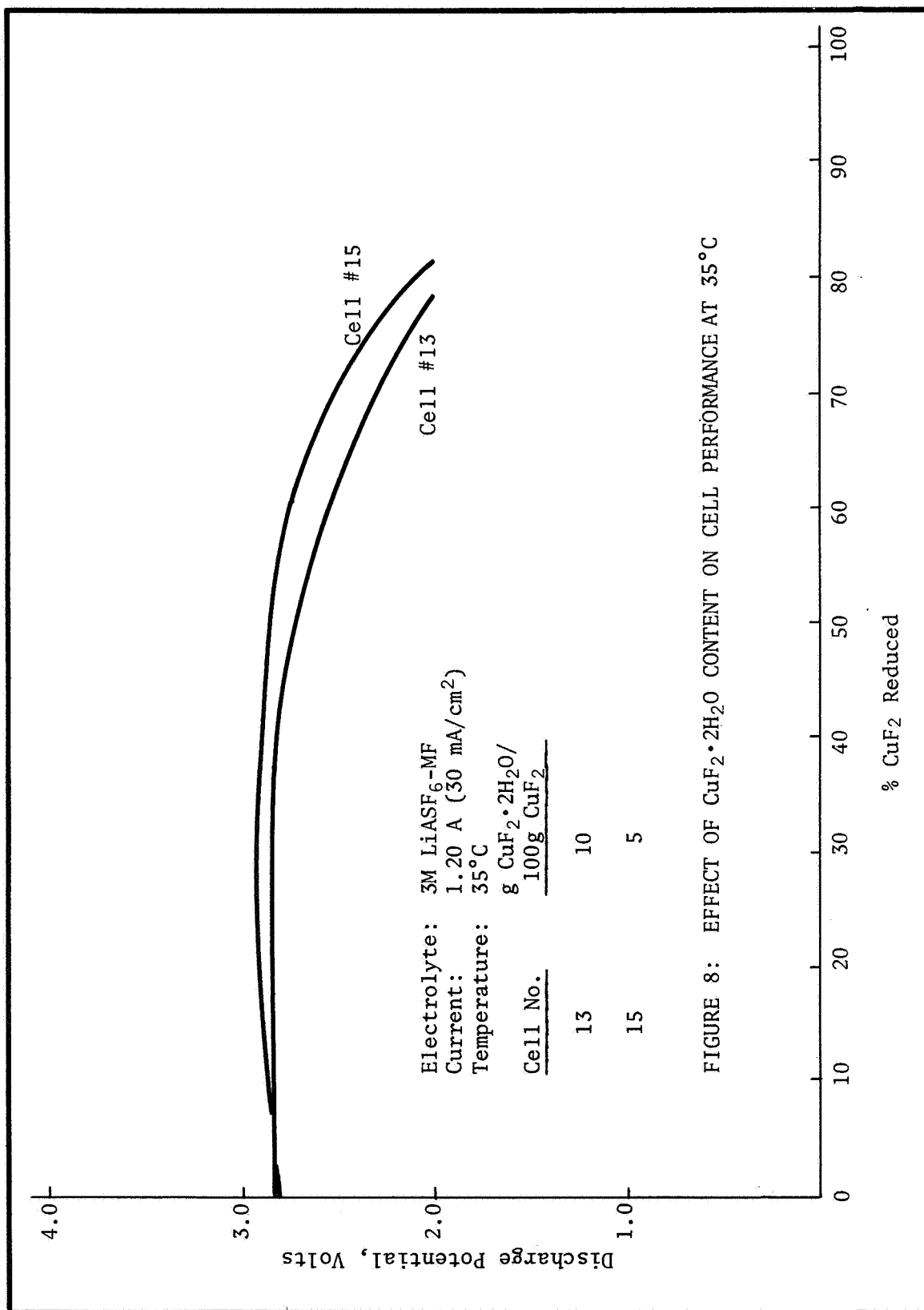


FIGURE 8

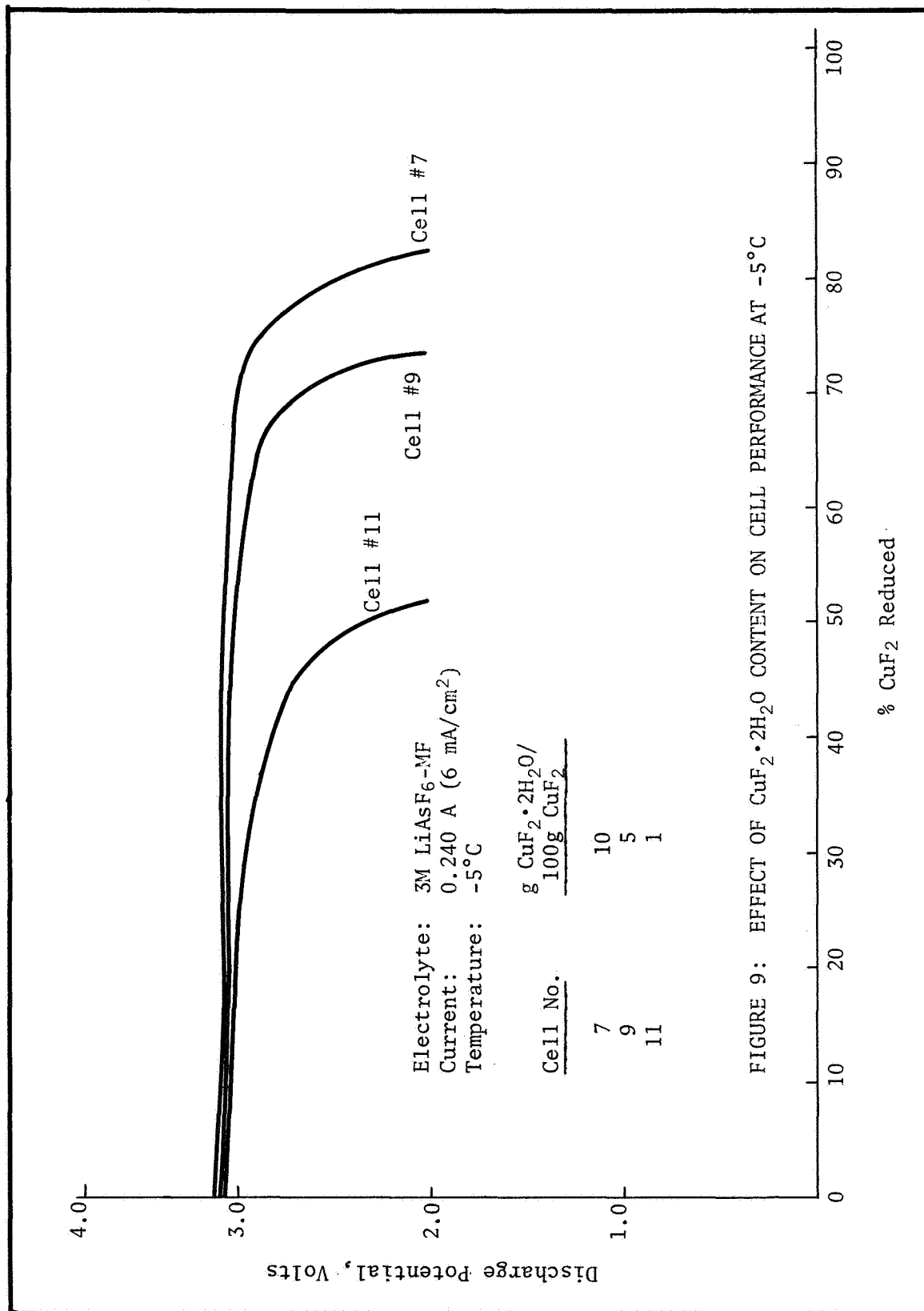


FIGURE 9

2. 3. 2. 4. Electrode Polarization Tests

In order to obtain anode and cathode polarization data, some cells were built with two working electrodes and a lithium reference electrode. The working electrode dimensions were 5/8 x 1-1/2 in. and were assembled between glass slides in a one inch I.D. glass tube. The separator was extended below the glass slides so it would be immersed in a pool of excess electrolyte in the tube; the lithium reference electrode likewise was immersed in the liquid. To eliminate IR polarization effects, the Kordes pulse current generator was employed.

Voltage-time curves for the better of two cells with each electrolyte are shown in Figures 10 - 12, pages 29 - 31. In all cells, the anode potential remained within 150 mv of OCV, and cell voltage drop resulted mainly from cathode polarization. These data again show that the MF cells are not anode limited, and the improved performance of LiAsF_6 over LiClO_4 is a result of better cathode performance.

2. 3. 3. Seven-Plate Cells

Test cells having three positive and four negative electrodes were built and discharged in order to gain experience with larger cell construction, and to obtain better estimates for the performance potential of the CuF_2 -Li couple with methyl formate electrolyte. Except for the larger number of electrodes used, construction of these cells was similar to that of the 3-plate units.

2. 3. 3. 1. Cells With LiClO_4 /MF Electrolytes

At the beginning of this contract period, 7-plate cells were tested (in triplicate) at 5 discharge rates and two temperatures to establish further the performance potential of the MF battery system. In these tests, 4M LiClO_4 electrolyte was used (the electrolyte of choice at the end of the previous contract). The CuF_2 electrodes contained 2% cellulose acetate binder and 10% graphite conductor, and the dihydrate content was adjusted to give a 5% water content in the positive electrodes.

In order to prevent solvent loss during discharge, the test cells were assembled in hermetically sealed glass pipes as shown in Figure 13, page 32. The cells were activated via a hypodermic needle after 2 hours dry stand at the test temperature, and discharge was commenced after 15 minutes of wet stand.

Results of the discharge tests are shown in Table IX, page 33, and the voltage-time data for the best cell in each group have been plotted in

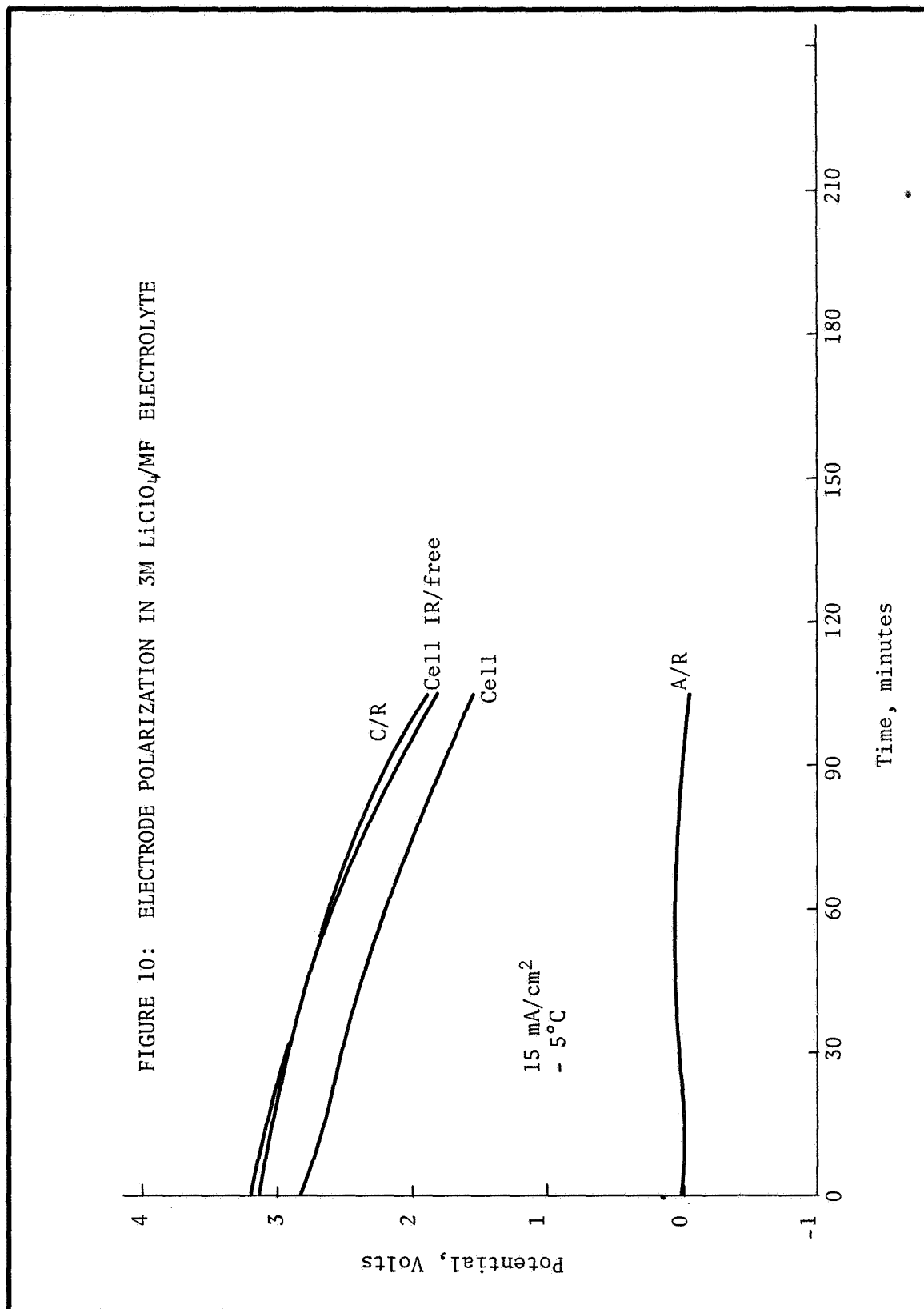


FIGURE 10

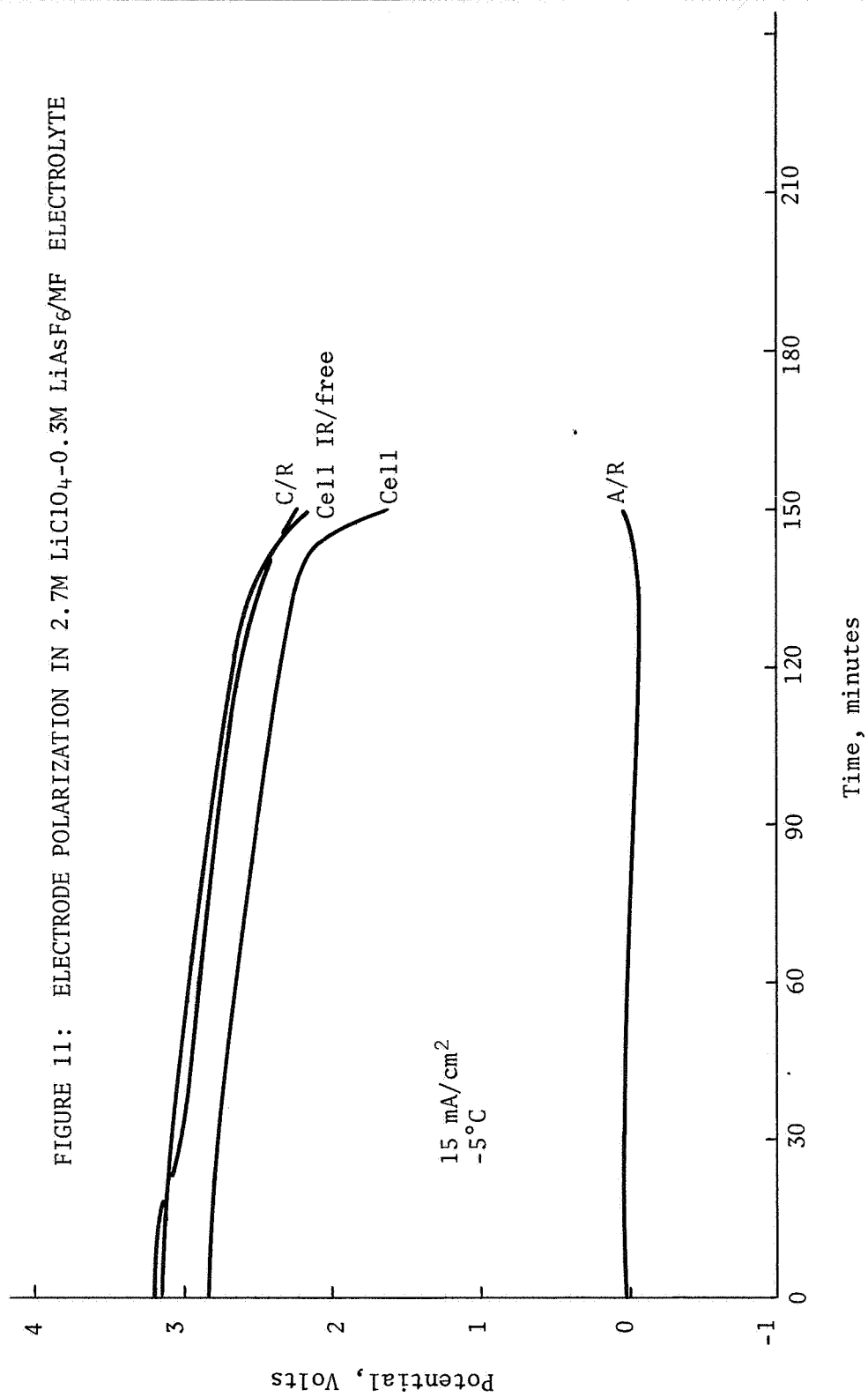


FIGURE 11

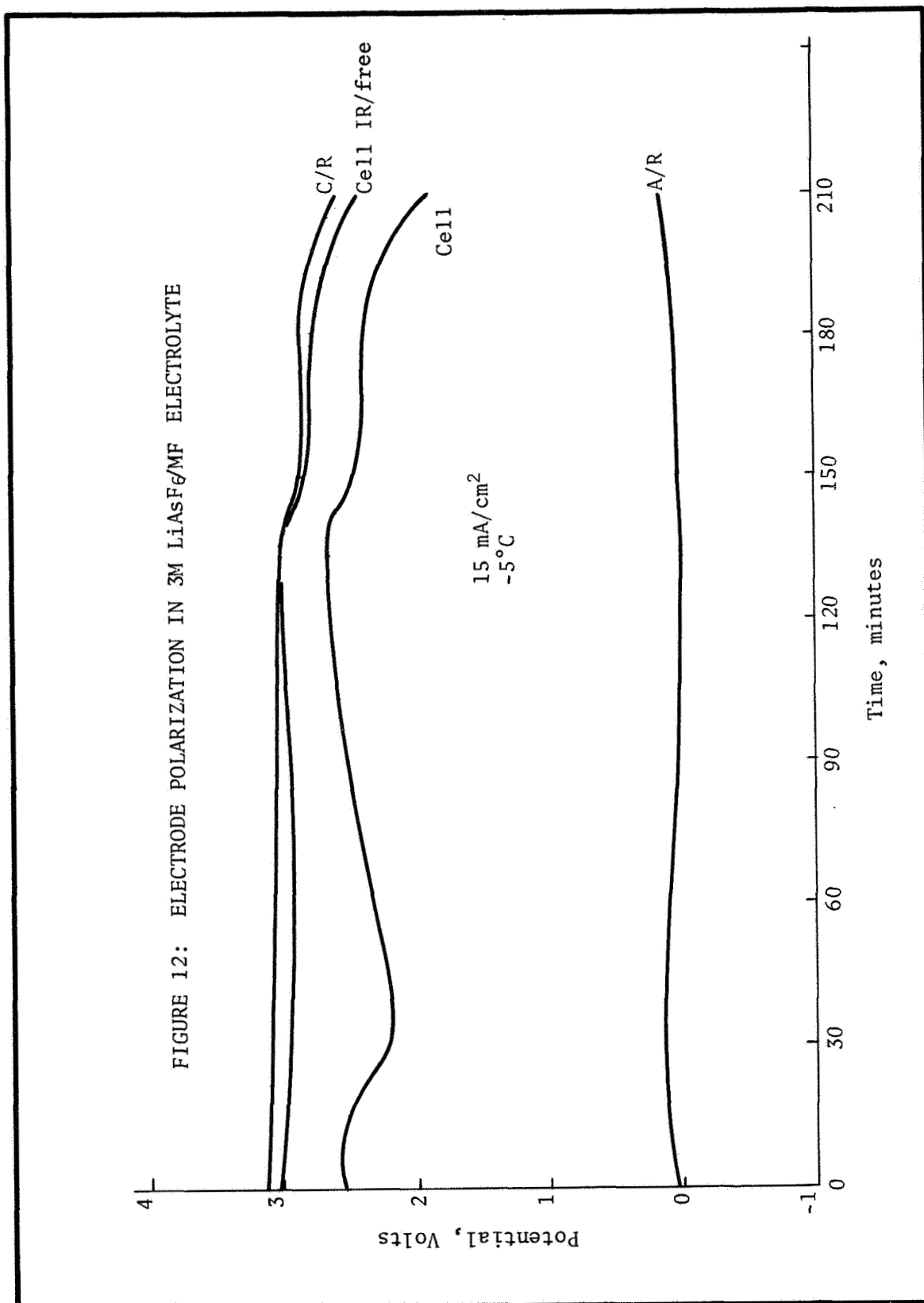
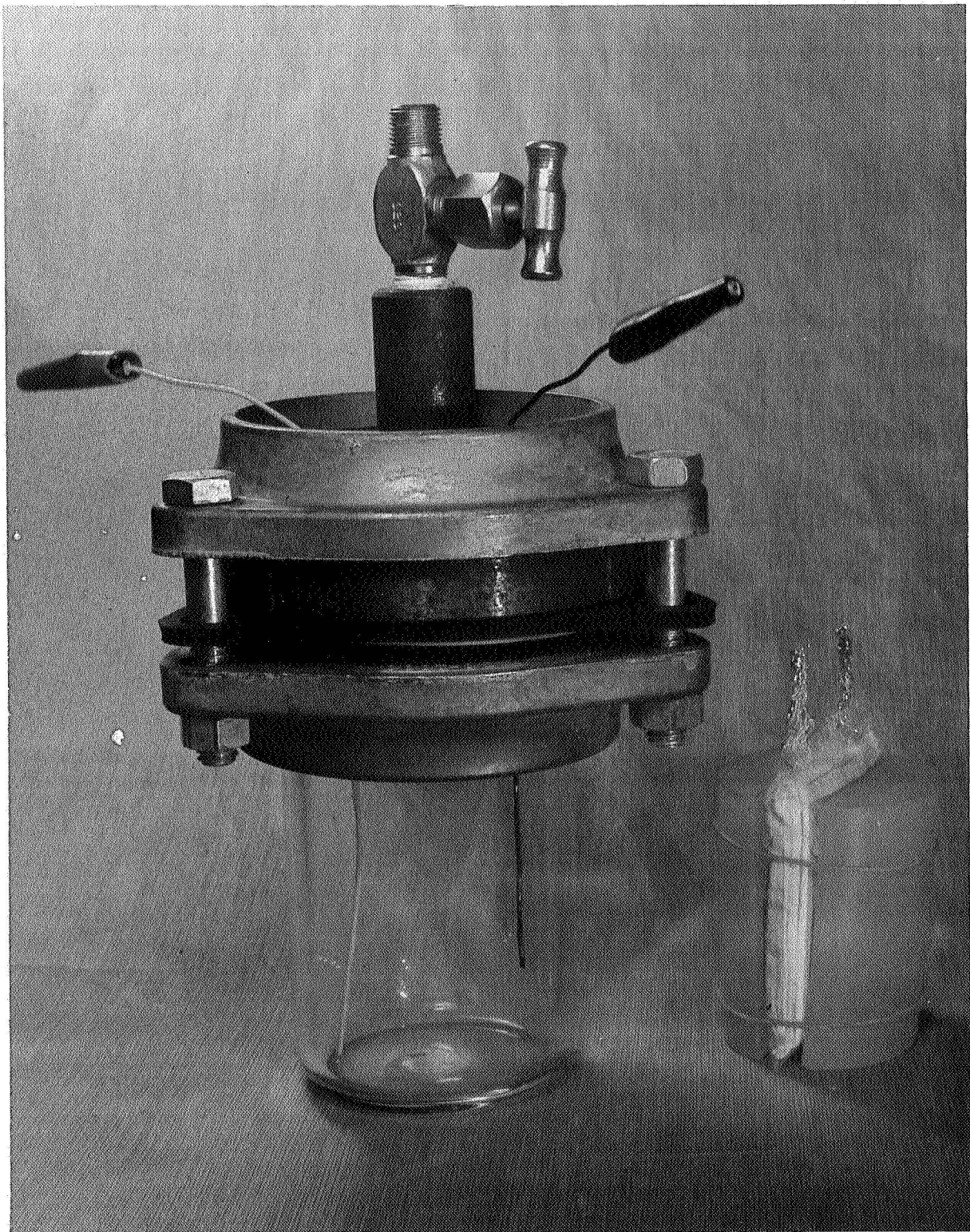


FIGURE 12



CELL DISCHARGE ASSEMBLY

FIGURE 13

TABLE IX

DISCHARGE PERFORMANCE OF $\text{CuF}_2\text{-Li}$ CELLS IN 4M LiClO_4/MF ELECTROLYTE

Cell No.	Theo. Cath., AH	Temp., °C	Current, A (mA/cm ²)	Initial C.C.V.	Average Dischg. Voltage	Time to 2.0 VF, Hours	Cathodic Eff., %
1	3.38	- 5	0.133	3.17	2.68	9.18	36.1
2	3.19	- 5	"	3.18	2.32	8.53	35.5
3	3.51	- 5	"	3.17	2.66	9.64	36.5
4	4.40	+35	0.133	3.24	2.97	15.00	45.4
5	4.56	+35	"	3.26	2.96	19.58	57.0
6	4.30	+35	"	3.31	2.95	16.78	51.9
7	4.15	- 5	0.350	3.15	2.75	5.30	44.8
8	4.26	- 5	"	3.13	2.76	6.06	49.8
9	4.17	- 5	"	3.08	2.78	5.95	50.0
10	4.37	+35	0.350	3.15	2.66	6.30	50.4
11	4.47	+35	"	3.13	3.00	7.75	60.8
12	4.34	+35	"	3.15	2.93	7.67	61.9
13	4.17	- 5	1.00	2.73	2.72	2.60	62.5
14	4.59	- 5	"	2.75	2.75	2.90	63.3
15	4.26	- 5	"	1.29	1.29	2.50	58.8
16	4.36	+35	1.00	2.99	2.78	1.87	42.8
17	4.32	+35	"	2.92	2.72	1.92	44.4
18	4.23	+35	"	2.98	2.83	2.60	61.6

TABLE IX (Continued)

DISCHARGE PERFORMANCE OF $\text{CuF}_2\text{-Li}$ CELLS IN 4M LiClO_4/MF ELECTROLYTE							
Cell No.	Theo. Cath., AH	Temp., °C	Current, A (mA/cm ²)	Initial C.C.V.	Average Dischg. Voltage	Time to 2.0 VF, Hours	Cathodic Eff., %
19	3.65	- 5	2.50	21.6	2.34	0.50	34.2
20	3.66	- 5	"	"	2.42	0.86	58.8
21	3.48	- 5	"	"	2.34	0.86	61.9
22	4.19	+35	2.50	21.6	2.59	0.51	30.3
23	4.63	+35	"	"	2.58	0.47	25.4
24	4.46	+35	"	"	2.64	0.35	19.6
25	3.85	- 5	4.00	34.5	2.27	0.38	39.5
26	3.81	- 5	"	"	1.67	0.55	57.7
27	3.97	- 5	"	"	2.14	0.43	43.3
28	4.35	+35	4.00	34.5	2.42	0.21	19.7
29	4.44	+35	"	"	2.28	0.30	27.0
30	4.29	+35	"	"	2.28	0.20	18.6

Figures 14 - 18, pages 36 - 40. The effect of discharge rate and temperature on the wh/lb obtained from these cells can be seen from the plot of energy/weight ratio vs discharge rate shown in Figure 19, page 41.

The best performance at -5°C (about 100 wh/lb) was obtained at about the 3-hour rate (8.6 mA/cm^2), but either increasing or decreasing the current caused a sharp drop in energy output. At the 35°C discharge temperature, the best performance was likewise at about the 3-hour rate. However, while the performance expectedly dropped off at higher discharge rates, lowering the current to the 20-hour rate did not significantly alter the energy output at this temperature. This output trend seems anomalous since one would expect the decrease in current to be more beneficial to the low temperature cells than to those at the higher temperature.

A possible explanation is that there may be some abrupt physical change (such as precipitation of the solute at the anode surface) at the lower temperature, which is eliminated by the temperature rise resulting from i^2R heating inside the cell at higher currents. This phenomenon should be researched in future work with electrode polarization studies at the temperatures and current densities of interest.

The highest container pressure observed during discharge was 10 psig at 2.5A and 35°C . For all other discharges, the pressure remained below this value.

2. 3. 3. 2. Cells With LiAsF_6 -MF Electrolyte

Another set of 7-plate cells was constructed and tested towards the conclusion of this program to further evaluate the better conductivity and Li stability of LiAsF_6 -MF electrolyte on cell performance.

The electrolyte solution for these tests was prepared as described in Section 2. 1. 1. 1., page 5. The positive plates were made to have the composition: CuF_2 - 100; $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ - 10; Conductex SC - 10; polystyrene - 1. The separation used was .015 in. glass filter mat, and the cells were assembled and discharged in the polyethylene test fixtures as shown in Figure 20, page 42. Construction and discharge data for the evaluation of 30 cells in this test are shown in Table X, page 43. Voltage-time data for the best cell (in terms of CuF_2 reduction efficiency) in each replicate set are plotted in Figures 21 - 26, pages 45 - 50. Figure 27, page 51, shows the effect of discharge rate on energy density at the two test temperatures.

At the higher test temperature (35°C), the best performance (about 75% cathode efficiency) was obtained at the 1 and 2 hour discharge rates (34 and 17 mA/cm^2 , respectively). At the lower temperature (-5°C), lower discharge rates gave higher cathode utilization figures (80 - 85% at 4.3 and 8.5 mA/cm^2). This trend can be expected because of the lower rate of dissolution of CuF_2 and decreased conductivity of the electrolyte at lower temperatures.

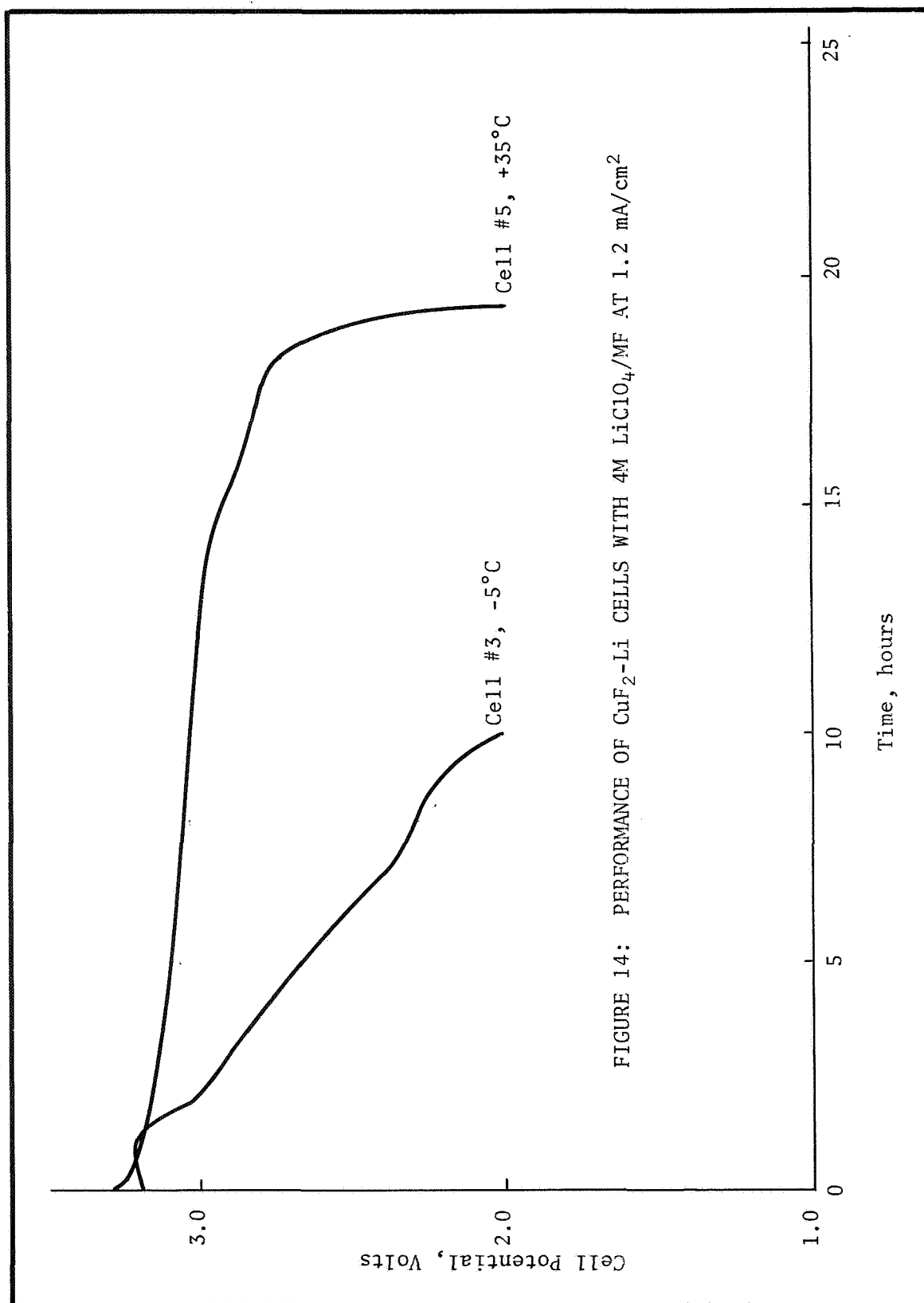


FIGURE 14

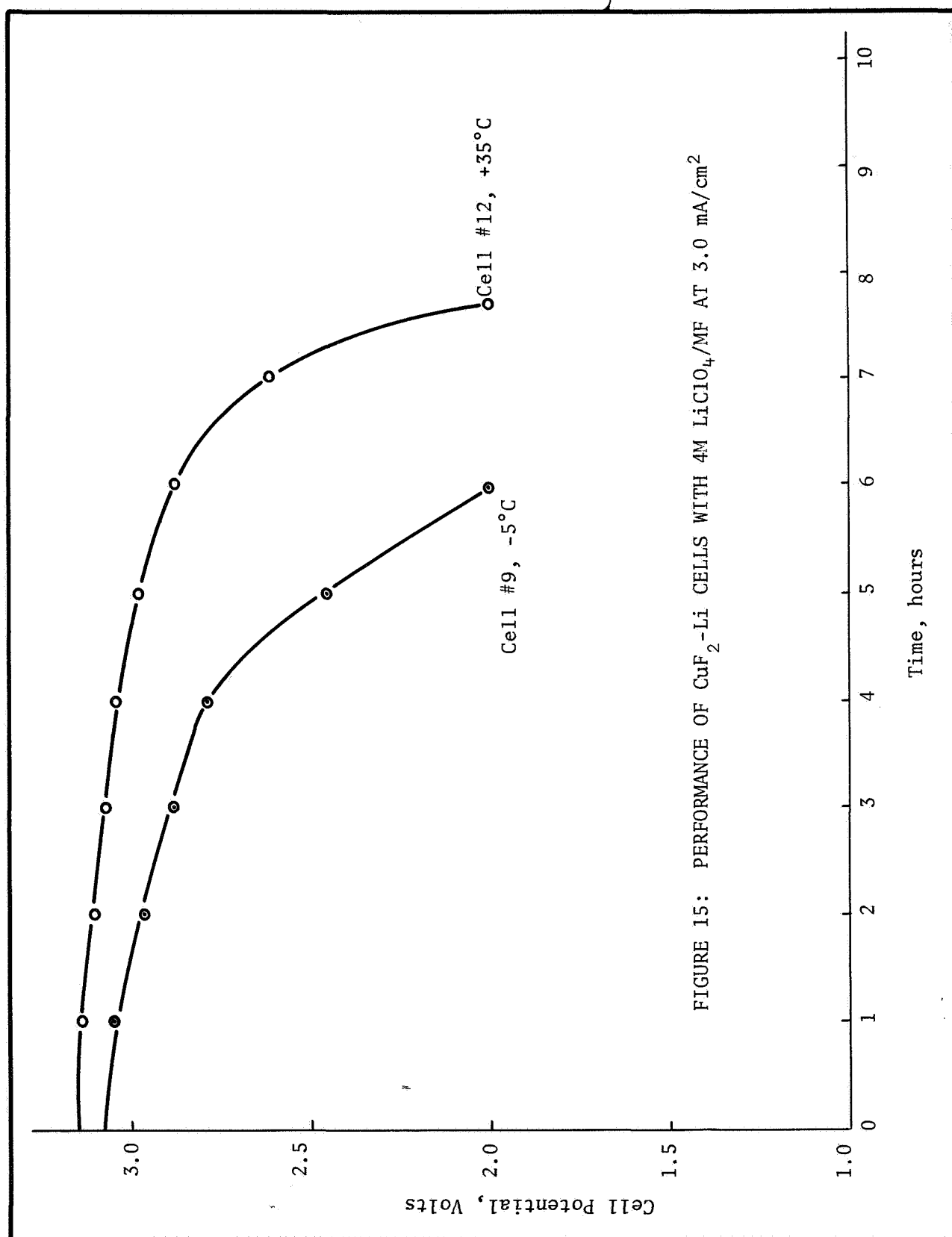


FIGURE 15: PERFORMANCE OF $\text{CuF}_2\text{-Li}$ CELLS WITH $4\text{M LiClO}_4/\text{MF}$ AT 3.0 mA/cm^2

FIGURE 15

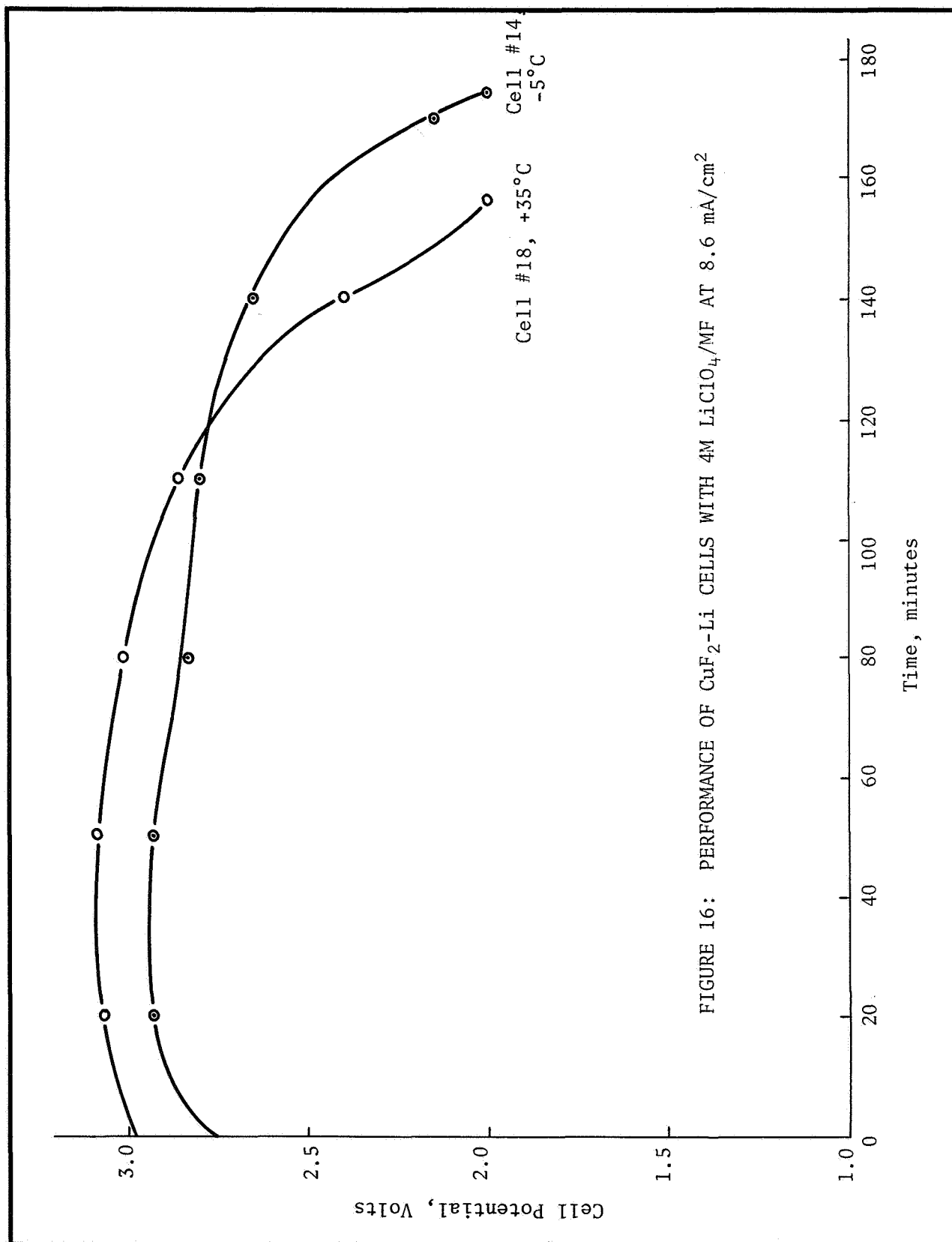


FIGURE 16: PERFORMANCE OF $\text{CuF}_2\text{-Li}$ CELLS WITH $4\text{M LiClO}_4/\text{MF}$ AT 8.6 mA/cm^2

FIGURE 16

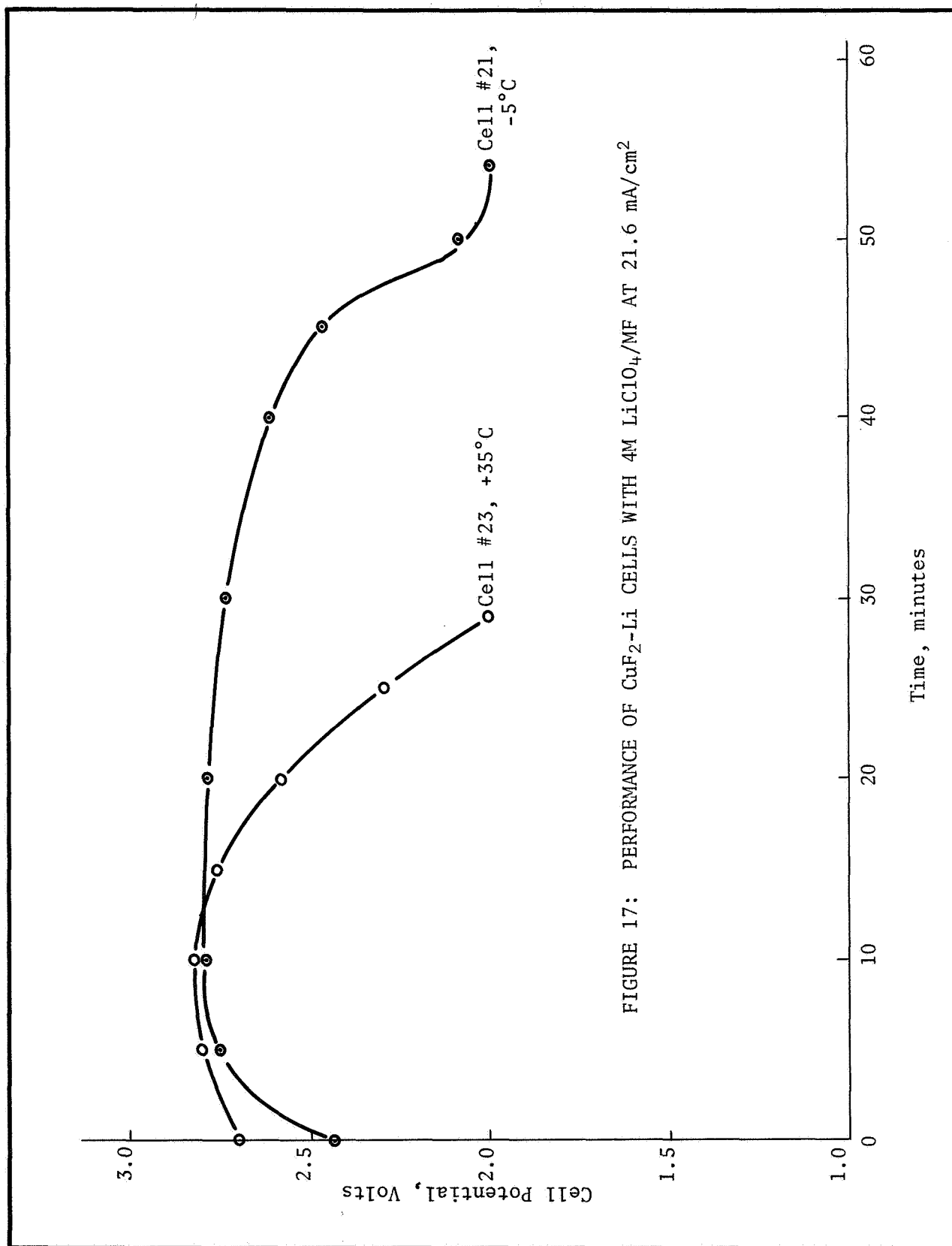


FIGURE 17: PERFORMANCE OF $\text{CuF}_2\text{-Li}$ CELLS WITH $4\text{M LiClO}_4/\text{MF}$ AT 21.6 mA/cm^2

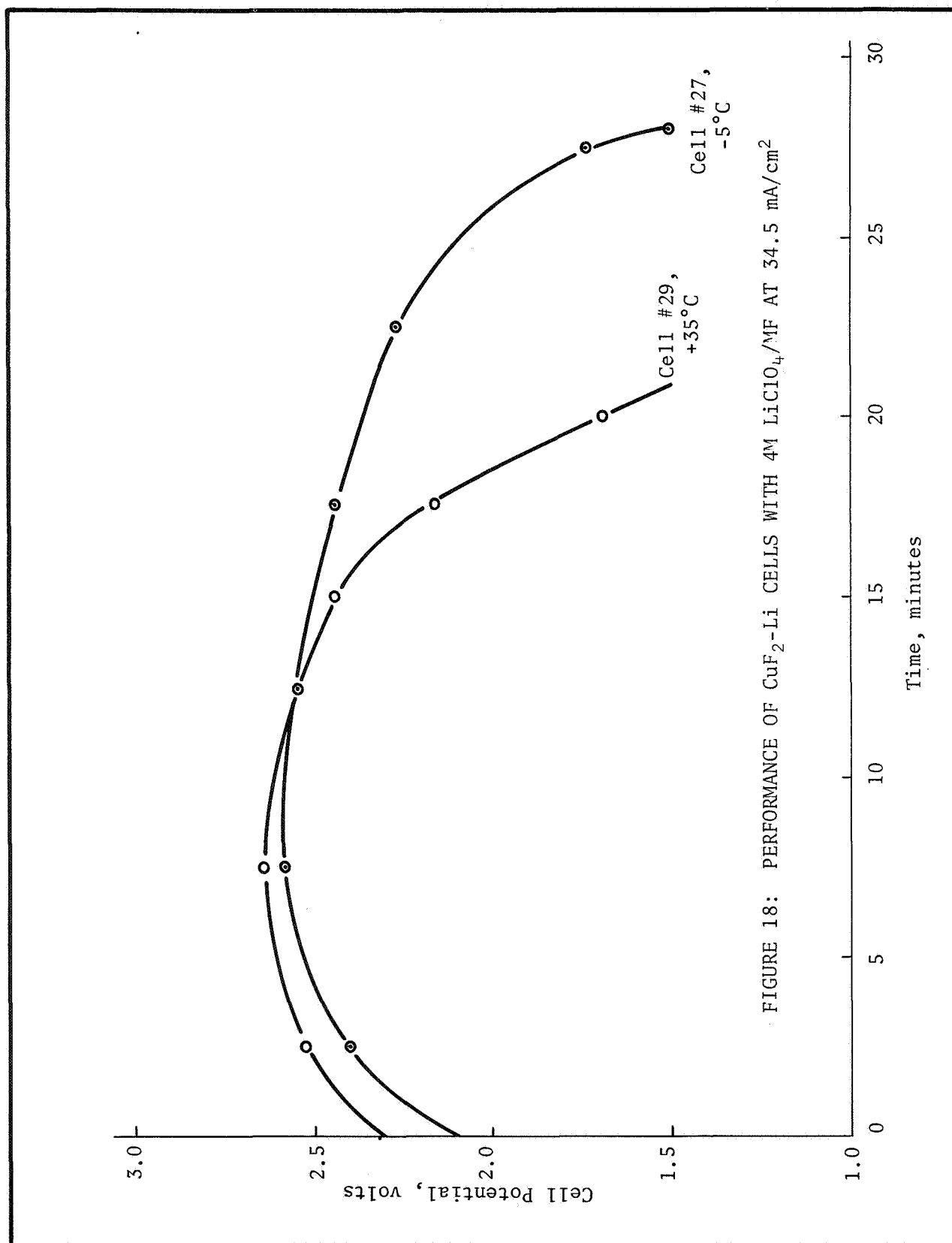


FIGURE 18

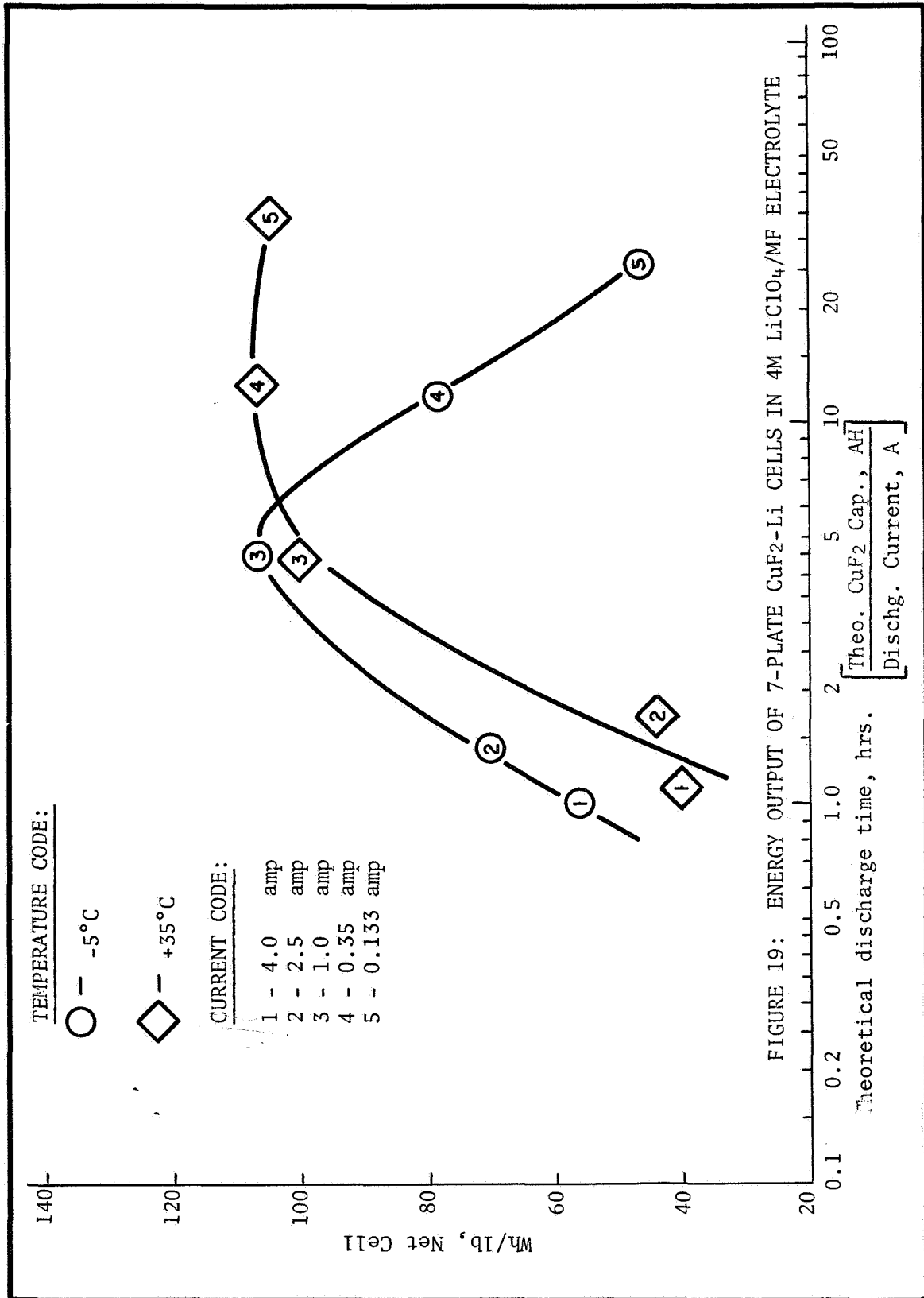
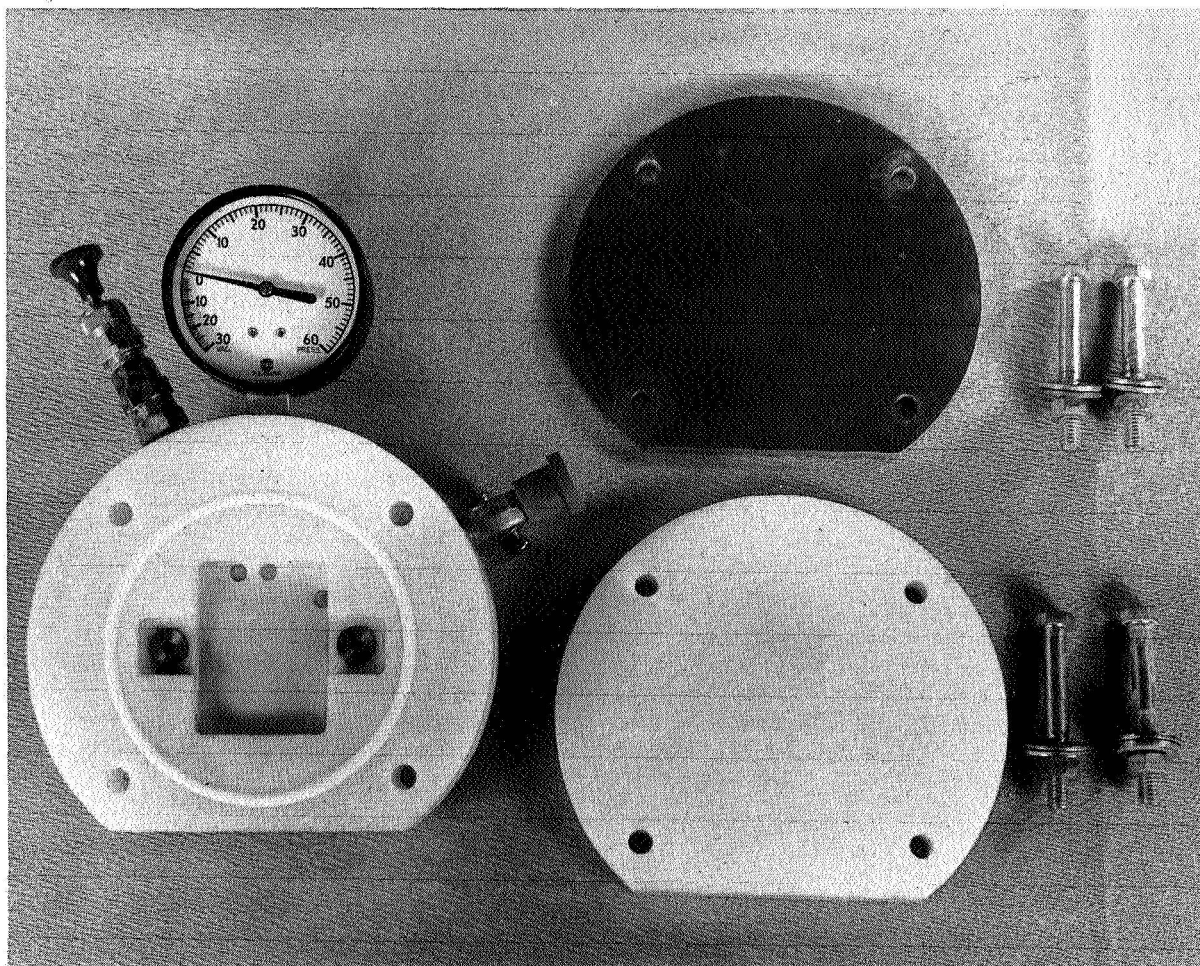


FIGURE 19



TEST FIXTURE FOR LiAsF₆ ELECTROLYTE CELLS
FIGURE 20

TABLE X

DISCHARGE PERFORMANCE OF $\text{CuF}_2\text{-Li}$ CELLS WITH 3M LiAsF_6/MF ELECTROLYTE

Cell No.	Theo. Cath., AH	Temp., °C	Current A	(mA/cm ²)	Initial C.C.V.	Average Dischg. Volts	Time to 2.0 VF, Hours	Cathodic Eff., %	Wh/lb net cell (best cell in each group)
1	5.38	+35	6.00	51.2	2.22	2.36	.42	46.5	91.7
2	4.50	"	"	"	1.99	2.22	.45	60.0	
3	5.22	"	"	"	2.22	2.38	.58	66.4	
4	5.40	+35	4.00	34.2	2.73	2.66	.95	70.2	112.3
5	5.08	"	"	"	2.70	2.66	.93	73.1	
6	4.87	"	"	"	2.72	2.63	.83	68.3	
7	5.62	+35	2.00	17.1	3.20	2.94	2.15	76.3	136.9
8	5.34	"	"	"	3.21	2.91	2.03	76.2	
9	4.59	"	"	"	3.17	2.67	1.13	49.1	
10	6.79	+35	1.00	8.5	3.26	3.05	4.43	65.2	138.2 (Internal Short)
11	6.06	"	"	"	0	0	0	0	
12	5.82	"	"	"	3.29	3.09	3.77	64.7	
13	5.84	+35	.50	4.3	3.20	2.90	2.16	18.3	64.7
14	5.62	"	.50	"	3.24	2.91	4.20	37.2	
15	5.94	"	.50	"	3.24	2.85	2.06	17.2	

TABLE X (Continued)

DISCHARGE PERFORMANCE OF CuF₂-Li CELLS WITH 3M LiAsF₆/MF ELECTROLYTE

Cell No.	Theo. Cath., AH	Temp., °C	Current A	(mA/cm ²)	Initial C.C.V.	Average Dischg. Volts	Time to 2.0 VF, Hours	Cathodic Eff., %	Wh/lb net cell (best cell in each group)
16	5.08	- 5	4.00	34.2	2.50	2.29	.75	59.3	92.4
17	6.51	- 5	"	"	2.69	2.54	1.02	62.4	
18	5.39	- 5	"	"	2.69	2.39	.88	65.2	
19	6.18	- 5	2.00	17.1	2.53	2.58	1.95	64.9	120.0
20	6.02	- 5	"	"	2.63	2.60	2.23	64.5	
21	6.46	- 5	"	"	2.66	2.59	2.25	69.4	
22	4.47	- 5	1.00	8.5	3.03	2.91	3.70	82.4	128.3
23	4.65	- 5	"	"	3.06	2.92	3.86	83.5	
24	4.74	- 5	"	"	3.05	2.93	3.96	83.3	
25	5.77	- 5	.50	4.3	3.10	2.91	9.58	83.9	149.8
26	5.33	- 5	.50	"	3.10	2.96	8.88	83.2	
27	4.96	- 5	.50	"	3.14	2.93	8.16	82.1	
28	4.33	- 5	.152	1.3	3.23	3.04	15.85	55.3	91.5
29	4.61	- 5	.152	"	3.23	2.99	20.48	66.2	
30	5.18	- 5	.152	"	3.23	2.93	20.71	58.3	

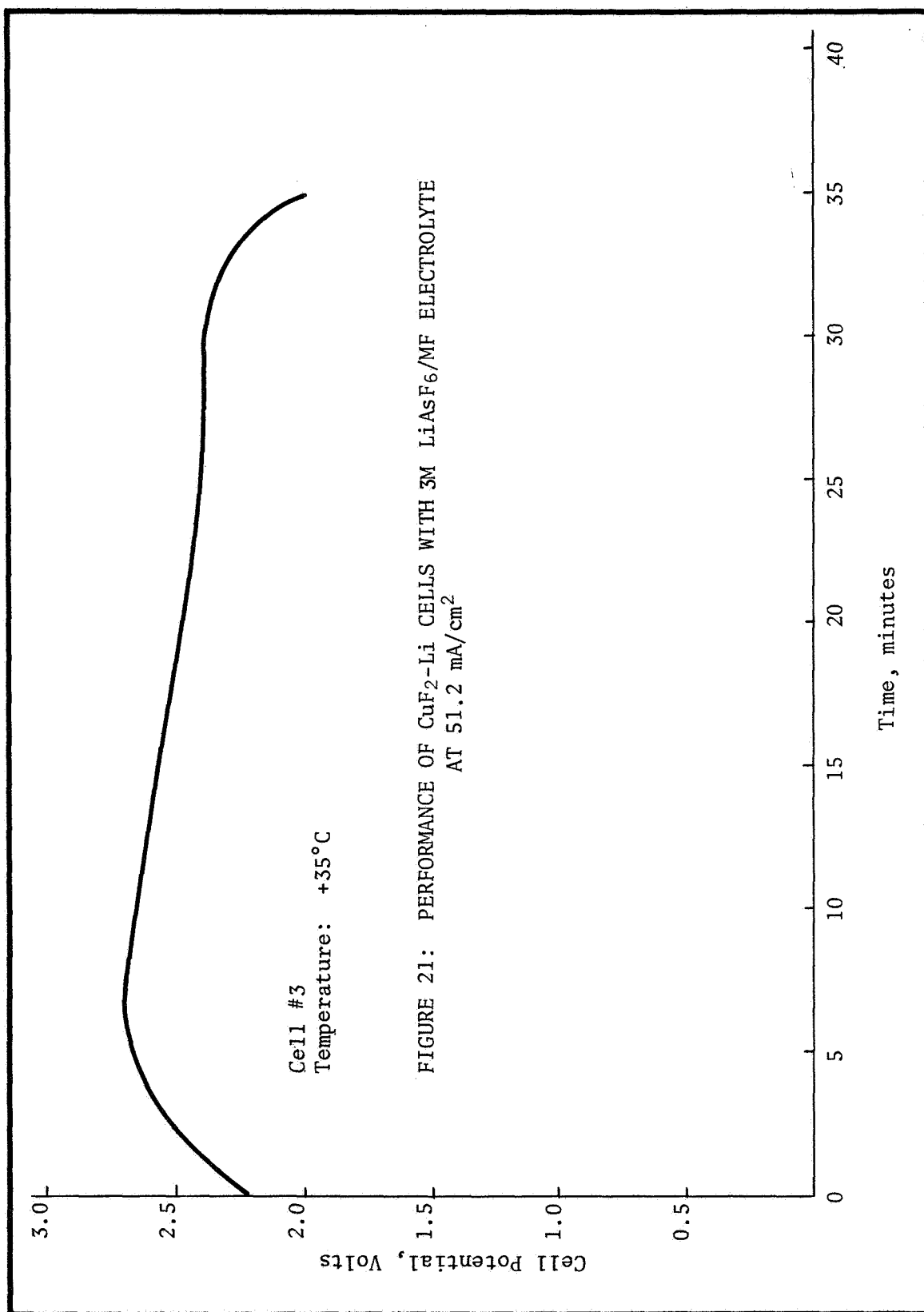


FIGURE 21

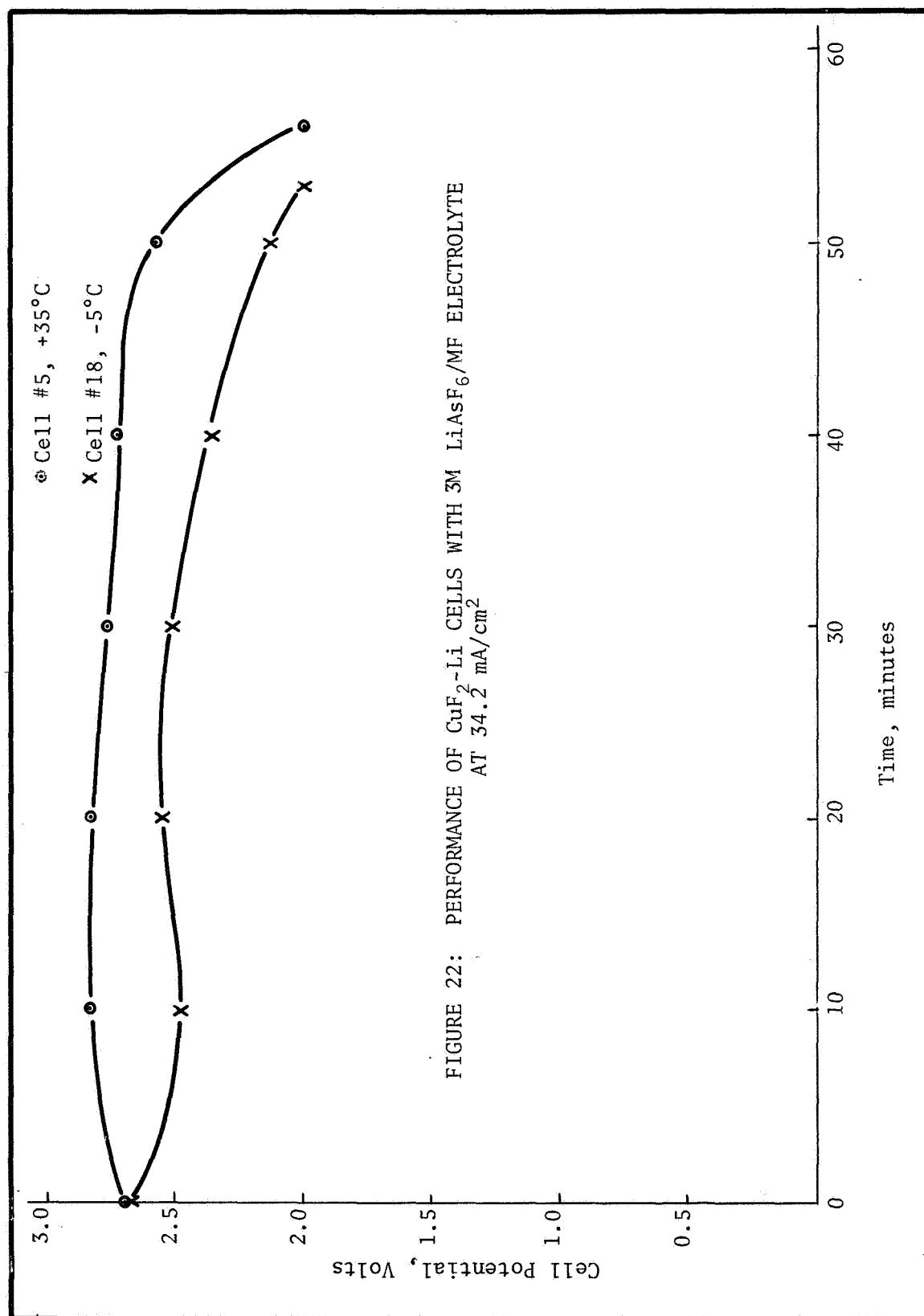


FIGURE 22

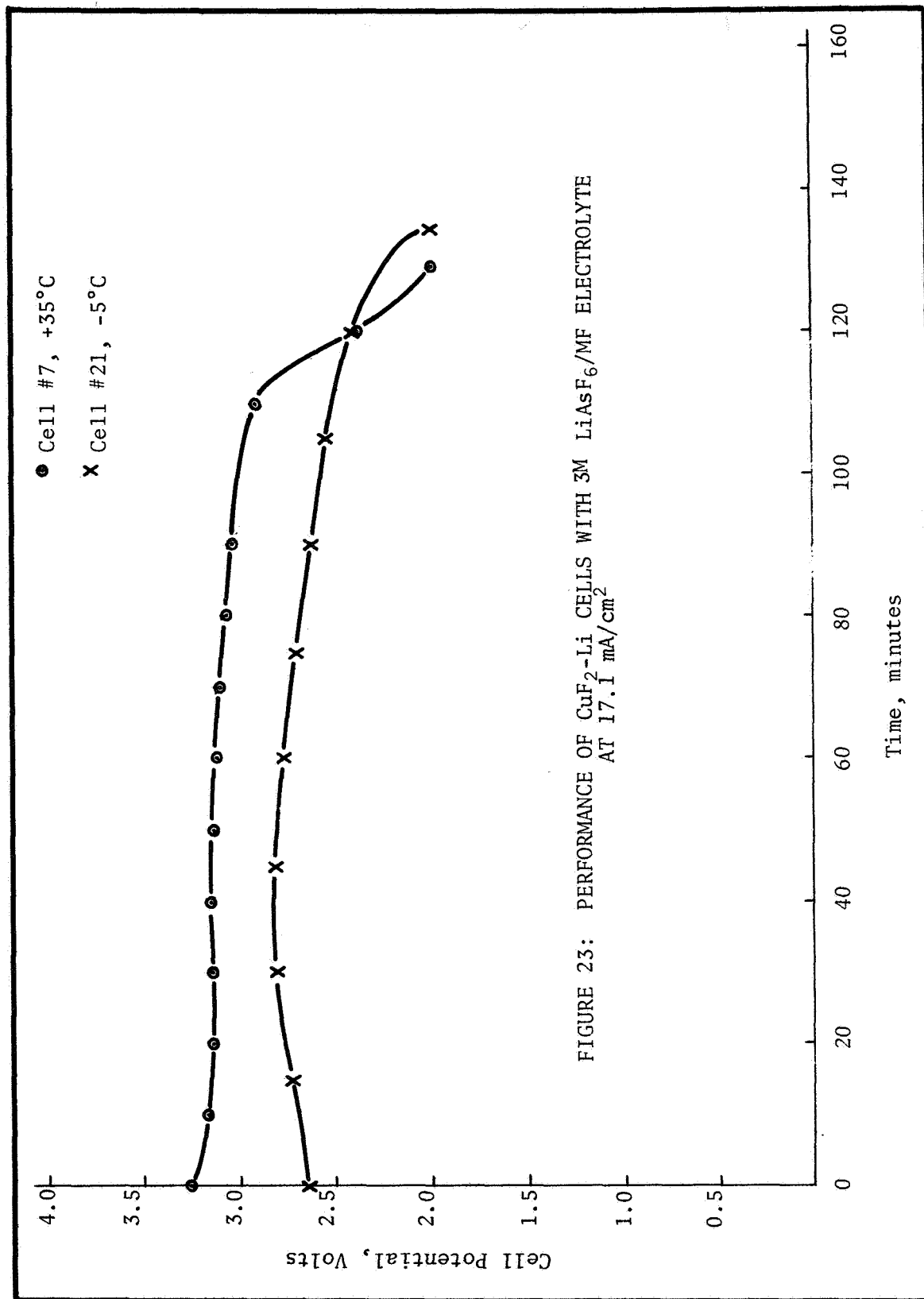


FIGURE 23

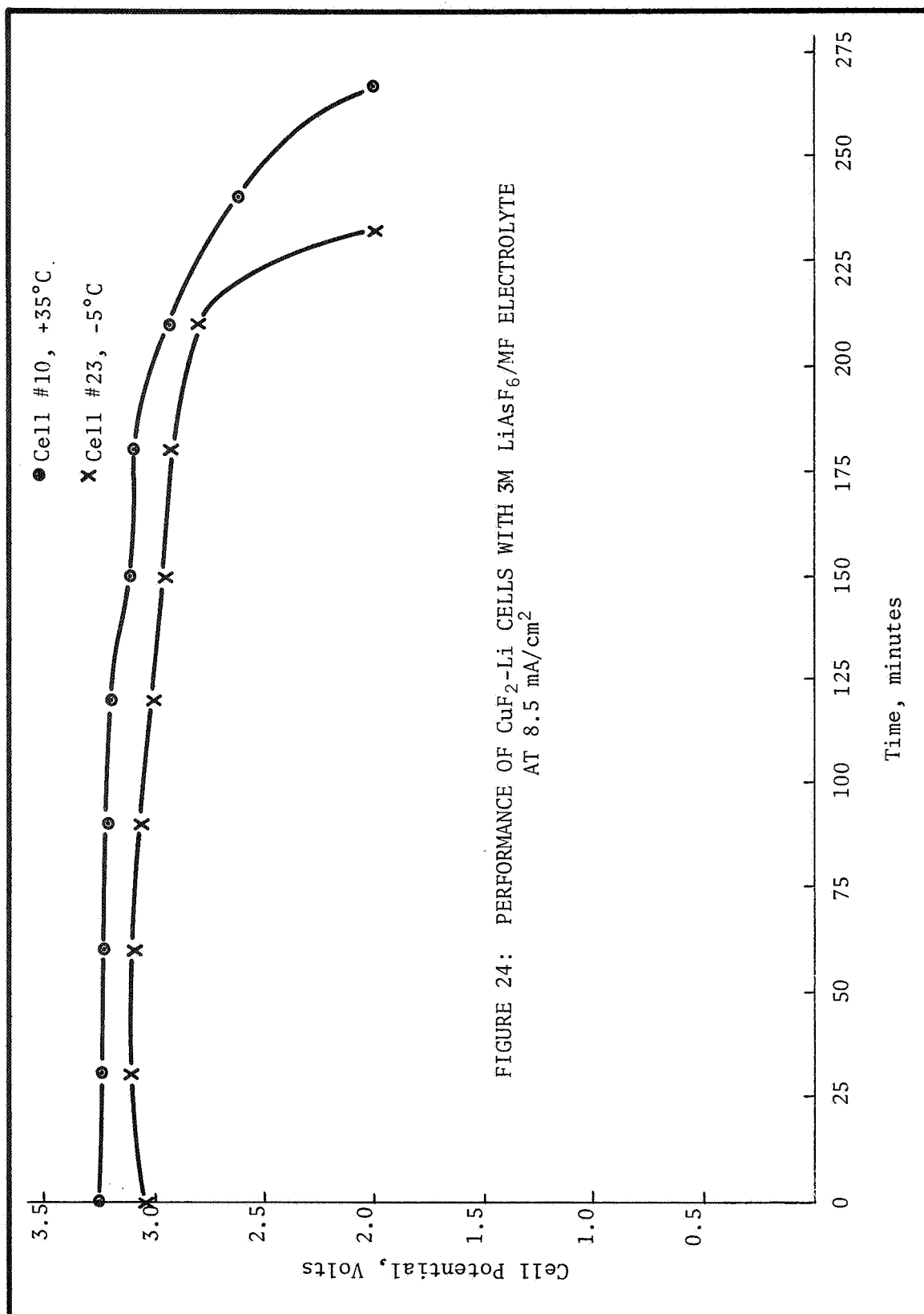


FIGURE 24

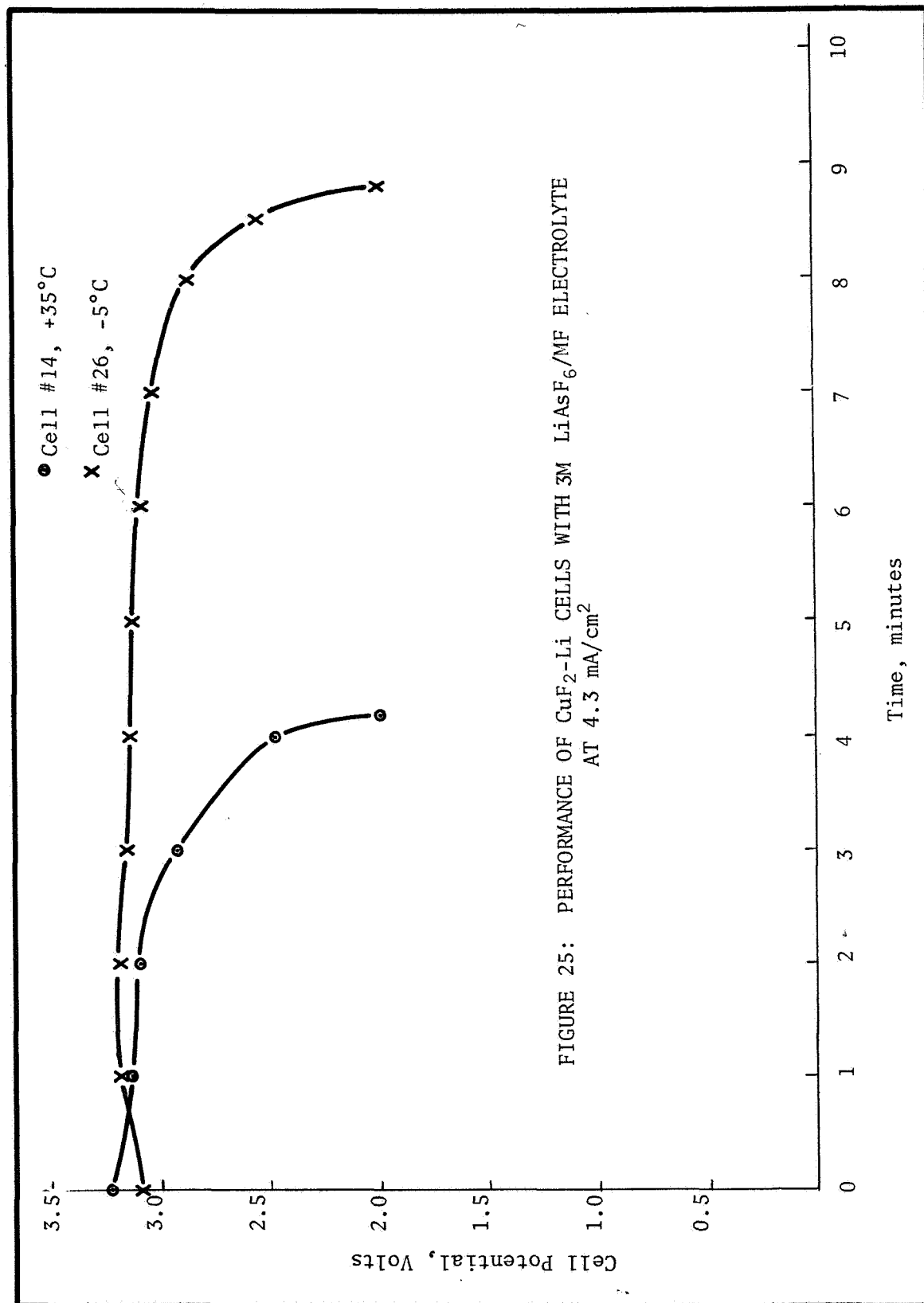


FIGURE 25

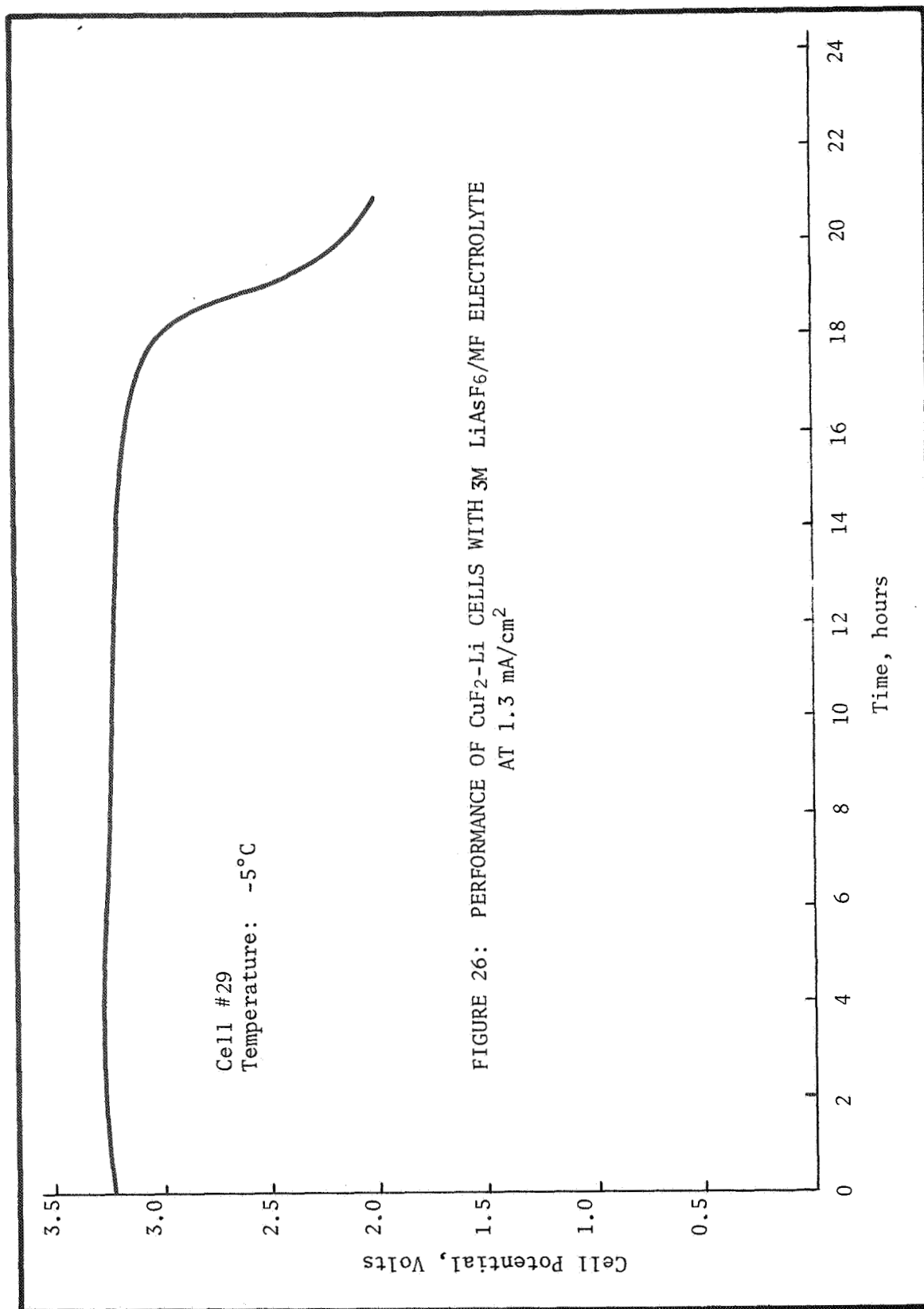


FIGURE 26

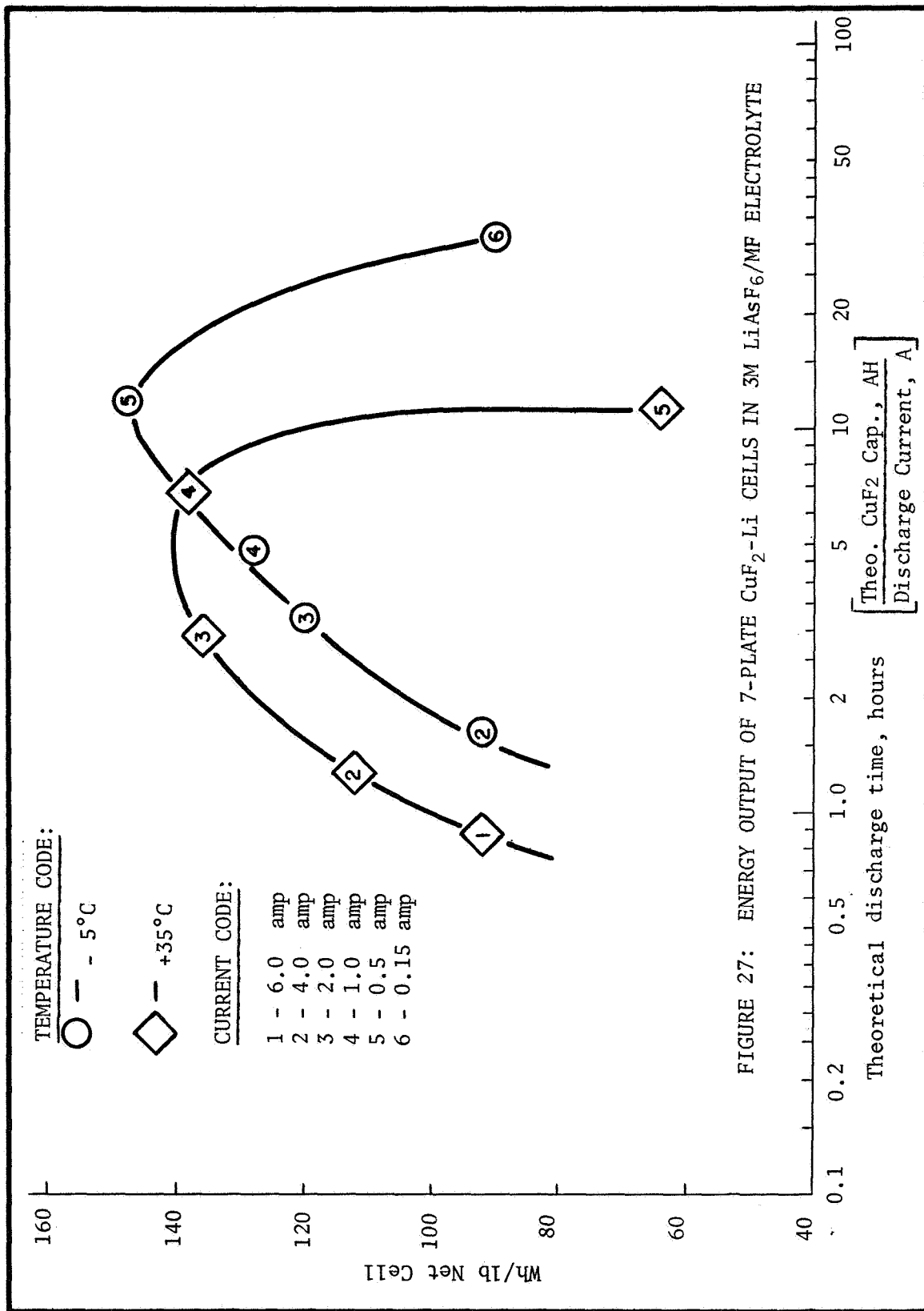
FIGURE 27: ENERGY OUTPUT OF 7-PLATE CuF_2 -Li CELLS IN 3M LiAsF_6 /MF ELECTROLYTE

FIGURE 27

All of the cells tested developed considerable pressures, which necessitated the installation of pressure relief valves on the discharge fixtures. By doing this, the overpressure on the cells was limited to 30 psi, which prevented distortion and damage to the test fixtures. The rate of pressure buildup was faster at the higher discharge rates and test temperature. Chromatographic gas analyses of samples collected from the relief valves showed the presence of hydrogen and methane, a somewhat unexpected result in view of the results of the test-tube compatibility tests of lithium in the LiAsF_6 -MF electrolyte. Apparently, the increased temperature and/or the continuous anodic regeneration of fresh lithium surface contribute to the continuous gassing of the cells. This condition will have to be considered in designing cell geometry and hardware for the system.

3. LOW RATE BATTERY STUDY

This section of the report describes work on the development of a long-life, high energy density, primary battery. This battery would have a non-reserve construction and a discharge life of 100 to 1000 hours.

3. 1. Compatibility Tests

Copper fluoride and lithium were the electrode materials of interest in the low rate battery program. Compatibility tests were, therefore, conducted with these materials in various candidate electrolyte solutions.

3. 1. 1. Preparation of Electrolytes

A considerable portion of the contractual effort on the low rate system was directed toward purification and treatment of materials so that the wet shelf life of the CuF_2 -Li system could be improved. In this section, purification of solvents and electrolyte solutes is described.

3. 1. 1. 1. Purification of Solvents

In general, the solvents used in this part of the program were purified by treatment with a strong reducing agent (e.g., LiAlH_4 or Li powder), followed by distillation at reduced pressure.

Lithium powder (1 - 1.5g/100 ml solvent) was used for the purification of propylene carbonate. Distillation was conducted at 1 - 5 mmHg pressure, rejecting the first and last tenth of the batch. Distillation thru an 18 in. Vigreux column was carried out without having to remove the lithium powder first. With careful application of this technique, water contents of less than 50 ppm (Karl Fischer analysis) were produced consistently.

Glyme and diglyme were treated with LiAlH_4 (2.5g/100 ml), rather than with Li powder. Trimethyl phosphate was distilled only, since acceptably low water contents (<100 ppm) could be produced without treating it with a reducing agent.

3. 1. 1. 2. Purification of Solutes

Candidate electrolyte salts were purified by recrystallization. Lithium perchlorate was precipitated from methyl formate solution (2 ml MF/g LiClO_4) by the addition of 1:1 dioxane-petroleum ether, and KPF_6 was precipitated from a 70:30 mixture of acetone and propylene carbonate (3.5 ml solvent/g of salt) by the addition of toluene. Other salts, including NaClO_4 , NaPF_6 , KAsF_6 , and KSbF_6 , were obtained from acetone (2 ml solvent/g of salt) by the addition of dioxane. After being washed with the precipitating solvent, the salts were vacuum dried at 110°C . The materials produced appeared to be free of any solvates and had water contents of less than 100 ppm (Karl Fischer analysis).

3. 1. 1. 3. Metathetical Preparations of Solutes

A number of electrolytes used in the low rate part of the program were prepared by double decomposition as described in Section 2. 1. 1. 3., page 6. In the report, these are identified by the suffix (m) after the chemical formula.

3. 1. 2. Lithium Stability in Electrolyte Solutions

Stability tests were conducted by immersing a $1/2 \times 1/16$ in. lithium strip in 5 - 10 ml of the test solution contained in a sealed test tube. The appearances of the test solution and lithium sample were used as the stability criteria in these tests.

3. 1. 2. 1. Effect of Solute Purification in 1M PC Solutions

A number of purified and unpurified candidate electrolyte salts were compared in propylene carbonate. (The salts which were not purified by reprecipitation were vacuum dried to below 100 ppm H_2O .) The appearance of the test samples after various exposure times is listed in Table XI, page 55.

Recrystallization of the salts effected no major change in lithium stability. The apparent displacement of sodium by lithium was noted for all sodium electrolytes; this does not appear to take place to any appreciable extent with the potassium electrolytes.

3. 1. 2. 2. Evaluation of Solvents with 1M LiBF_4

In this test, the Li stability in a number of solvents was compared to that in PC. Lithium fluoroborate was used as the solute because of its apparently high purity as received from the vendor.

TABLE XI

LITHIUM STABILITY TESTS IN 1M P.C. ELECTROLYTES AT +35°C

Solute	Recrystallized	APPEARANCE			
		100 Hours	200 Hours	500 Hours	1000 Hours
LiClO ₄	Yes	Li shiny, sol'n colorless.	No change.	No change.	No change.
LiClO ₄	No	Li shiny, sol'n colorless:	No change.	No change.	No change.
NaClO ₄	Yes	Gray-brown powder slowly coagulating & sinking. Li shiny & sol'n colorless.	No change.	No change.	Brown gelatinous material forming on liquid's surface. Li shiny & sol'n colorless.
NaClO ₄	No	Gray-brown powder completely coagulating & on bottom of sol'n. Li shiny & sol'n colorless.	No change	No change	Same as recrystallized except larger quantity of brown gelatinous material.
KAsF ₆	Yes	Li shiny & sol'n colorless.	No change.	No change.	Slight lithium surface blackening. No ppt & sol'n colorless.
KAsF ₆	No	Slight dulling on Li surface, sol'n colorless.	No change.	No change.	No change on Li surface. Small amount of white ppt in tube.
LiBF ₄	No	Li shiny, sol'n colorless.	No change.	No change.	No change.

TABLE XI (Continued)

LITHIUM STABILITY TESTS IN 1M P.C. ELECTROLYTES AT +35°C

Solute	Recrystallized	APPEARANCE			
		100 Hours	200 Hours	500 Hours	1000 Hours
NaPF ₆	Yes	Gray-brown powder floating on liquid. Li shiny & sol'n colorless.	Gray-brown powder coagulating. Quantity didn't increase. Li shiny, sol'n colorless.	Gray-brown coagulated material beginning to sink.	Blue fluorescent coating beginning to form on Li surface.
NaPF ₆	No	Same as recryst., except slightly more gray-brown powder.	Same as recrystallized.	Same as recryst.	Same as recryst.
KPF ₆	Yes	Li shiny, sol'n colorless.	Very slight dulling of Li. Sol'n colorless.	Edges of Li beginning to darken.	Li slightly more dull than 500 hrs.
KPF ₆	No	Li slightly dull, sol'n colorless.	Li surface slightly duller than 100 hrs. Sol'n colorless.	Same as recryst.	Li slightly duller than 500 hrs. & black coating beginning to form on Li above surface.
KSbF ₆	Yes	Black area forming on Li surface under liquid. Sol'n colorless.	No change.	No change.	Black forming on Li above liquid.
KSbF ₆	No	Same as recryst., except black area covers 1/2 of metal below liquid surface.	No change.	Black forming on Li above liquid. Small amount of white gelatinous ppt forming.	Li very black above liquid surface.

Results obtained from these stability tests are listed in Table XII, page 58. Propylene carbonate gave the most inert solution; the other three solvents tested appeared to offer no advantage in this respect.

3. 1. 3. Solubility of CuF_2 and $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ in Various Solvents

Extraction with an organic solvent was considered as a possible means for purifying CuF_2 . It was believed that a solvent which would preferentially dissolve $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, while leaving the anhydrous CuF_2 undissolved, would be useful for this purpose.

Solubility data for CuF_2 and $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ in a number of solvents were obtained as described in Section 2. 1. 3, page 8. Results of the Cu II analyses are shown in Table XIII, page 59.

Both DMF and DMSO showed higher solubility for the dihydrate by a factor of 30 - 100. The latter of the two solvents appeared to be more practical for purification purposes because dissolution of CuF_2 occurred in a shorter period of time. Ethanol and methanol showed lower solubility ratios between the two materials studied.

3. 1. 4. Copper Fluoride Treatment

The purity of the CuF_2 used in the low rate task of the program was a major concern. Control of this material's quality was maintained by X-ray analysis.

As received from the vendors, the CuF_2 typically had a $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ content of under 1%, with no other impurities being detectable by X-ray analysis. In addition, an "ultra-pure" material (for which spectrographic analysis was obtained), and the "typical" material treated with gaseous fluorine, were also evaluated. The latter was obtained by passing the gas thru CuF_2 maintained at 250°C until evolution of gases other than fluorine could not be detected (this work was performed at Temple Research Inst., Philadelphia, Pa.).

3. 1. 5. CuF_2 Stability in Electrolyte Solutions

Stability of CuF_2 in candidate electrolytes was determined as described in Section 2. 1. 3, page 8, except exposure times of up to 1000 hours were used in the low rate phase of the program. Low solubility for CuF_2 was assumed to be a requirement for any electrolyte system to be useful for long life cells.

TABLE XII

LITHIUM STABILITY IN 1M LiBF₄ AT +35°C

Solvent	Electrolyte, H ₂ O, ppm	APPEARANCE		
		24 Hours	500 Hours	1000 Hours
P.C.	125	Li shiny, sol'n colorless.	No change.	Very slight dulling of Li surface. Sol'n colorless.
TMP	83	One side & top edge of Li darkening. Sol'n colorless.	Li becoming very dark. Sol'n clear, light yellow.	Sol'n more yellow than at 500 hrs., otherwise no change.
G	139	Slight dulling of Li surface. Sol'n colorless.	1/3 of solvent evaporated thru serum stopper. Sol'n pale yellow. Li surface slightly dull.	Only a trace of solvent left. Liquid yellow-brown. Small amount of white solid in liquid. No change in Li appearance.
DG	100	Li shiny, sol'n colorless.	No change.	1/3 of solvent evaporated thru serum stopper. Sol'n very pale yellow. No change in Li appearance.

SOLVENT CODE:

P.C. - Propylene carbonate
T.M.P. - Trimethyl phosphate
G - Glyme
DG - Diglyme

TABLE XIII

CuF₂* AND CuF₂•2H₂O** SOLUBILITIES IN VARIOUS SOLVENTS AT +35°C

Solvent	Salt	Solvent H ₂ O µg/ml	Cu ⁺⁺ Concentration, (µg/ml)						
			24 Hrs.	1 Wk.	2 Wks.	3 Wks.	4 Wks.	5 Wks.	6 Wks.
DMF	---	57	0	0	0	0	0	0	0
DMF	CuF ₂	57	96	96	128	96	83	64	128
DMF	CuF ₂ •2H ₂ O	57	141	96	1248	6370	6290	7700	7200
DMSO	---	100	0	0	0	0	0	0	0
DMSO	CuF ₂	100	109	173	64	192	128	224	224
DMSO	CuF ₂ •2H ₂ O	100	102	7550	6930	6710	5540	7650	4380
EtOH	---	565	0	0	0	0	0	0	0
EtOH	CuF ₂	565	60	77	51	N.T.	N.T.	N.T.	N.T.
EtOH	CuF ₂ •2H ₂ O	565	74	339	1010	1401	1152	1120	928
MeOH	---	565	0	0	0	0	0	0	0
MeOH	CuF ₂	565	1108	1587	1789	N.T.	N.T.	N.T.	N.T.
MeOH	CuF ₂ •2H ₂ O	565	1540	1580	1570	1933	N.T.	1680	1698

* CuF₂, Lot KW-4-105, Ozark-Mahoning (0.9% CuF₂•2H₂O)**CuF₂•2H₂O, Lot KW-4-54, Ozark-Mahoning (approx. 95% CuF₂•2H₂O)

N.T. = No test.

3. 1. 5. 1. Effect of Purified Electrolyte Salts

Results of CuF_2 solubility tests in 1M' solutions of various purified and unpurified salts in propylene carbonate are shown in Table XIV, page 61. In general, recrystallization reduced the amount of Cu II in solution, particularly in the case of K- and Na- salts (the high value obtained for recrystallized KPF_6 appears to be erratic and was probably caused by contamination of the test specimen).

3. 1. 5. 2. Effect of Solvent

The solubility of CuF_2 in 1M' LiBF_4 solutions in PC (propylene carbonate), TMP (trimethyl phosphite), G (glyme), and DG (diglyme), was determined. The results of the Cu II analyses for this test series are shown in Table XV, page 62. Considerably lower solubility figures were obtained in TMP than in the other three solvents. This phenomenon may be connected with the observation that copious quantities of LiF are soluble in TMP (more than 15 mols/L). Even though conductivity measurements indicate that the salt is not ionized, sufficient fluoride ion concentration may be generated to depress dissolution of CuF_2 .

3. 1. 5. 3. Effect of CuF_2 Source and Treatment With F_2

If small amounts of impurities affect the stability of CuF_2 in the electrolyte, materials from various manufacturers as well as purified materials should show differences in electrolyte solubility. In this test, however, little difference in solubility trend in 1M LiClO_4/PC electrolyte was observed, as can be seen from the data in Table XVI, page 63. These results indicate that small amounts of impurities probably have little effect on the dissolution of CuF_2 in electrolytes having a low water content.²

3. 1. 5. 4. Effect of Extraction With Dimethyl Sulfoxide

Since DMSO was demonstrated to be a good solvent for $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, the possibility of purifying CuF_2 by extraction with this liquid was studied further. Ten grams of CuF_2 were extracted with 100 ml of DMSO for two weeks, washed with benzene, and vacuum dried. The solubility of this material in 1M' LiClO_4/PC electrolyte was compared with that of the

²The effect of water on solubility of CuF_2 in LiClO_4 -PC electrolytes was studied in earlier work - see S. Abens, et. al., NASA CR-72331, pp. 12 - 18.

TABLE XIV

SOLUBILITY OF CuF_2 IN VARIOUS IM P.C. ELECTROLYTES

Propylene Carbonate: MC & B, Distilled from Li powder
 Salts: Vacuum dried 18 hours at 110°C
 Cupric Fluoride: Ozark-Mahoning, Lot KW-4-105;
 0.9% $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, untreated
 Temperature: $31 - 35^\circ\text{C}$

Solute	Recrystallized	Electrolyte H_2O , ppm	Cu^{++} Concentration, ($\mu\text{g}/\text{ml}$)			
			24 Hours	200 Hours	300 Hours	1000 Hours
LiClO_4	No	65	51	115	180	320
LiClO_4	Yes	65	<25	128	269	538
KAsF_6	No	72	51	57	58	109
KAsF_6	Yes	50	<25	<25	<25	<25
NaClO_4	No	54	38	64	82	115
NaClO_4	Yes	48	<25	<25	<25	<25
KSbF_6	No	113	<40	74	62	295
KSbF_6	Yes	105	<40	<40	<40	<40
KPF_6	No	167	<40	135	135	62
KPF_6	Yes	99	<40	<40	62	1845
NaPF_6	No	138	<40	<40	<40	215
NaPF_6	Yes	109	<40	<40	<40	62
LiBF_4	No	65	89	192	263	333

TABLE XV
SOLUBILITY OF CuF_2 IN VARIOUS IM ELECTROLYTES

Solvents: Glyme: MC & B, Lot 22, distilled from LiAlH_4
Diglyme: MC & B, Lot 11, distilled from LiAlH_4
Trimethylphosphate: MC & B, Lot 10, Practical Grade,
distilled at 2.5 mmHg
P.C.: MC & B, Lot 14, Li treated and distilled at 0.2 mmHg

Salts: LiBF_4 : Vacuum dried 18 hours at 110°C

CuF_2 : Ozark-Mahoning, Lot KW-4-105, 0.9% $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, untreated

Temperature: $31 - 33^\circ\text{C}$

Solvent	Electrolyte, H_2O , ppm	Cu^{++} Concentration, ($\mu\text{g}/\text{ml}$)		
		24 Hours	200 Hours	500 Hours
P.C.	125	1388	1440	1780
TMP	83	141	218	448
G	139	3575	3660	4710
DG	100	2750	2590	2680
				1963
				256
				8070
				4480

TABLE XVI

SOLUBILITY OF COPPER FLUORIDE IN 1M LiClO₄/PC ELECTROLYTE

CuF₂: 1.0g of indicated grade
 Electrolyte: 0.04 mols of LiClO₄ in 40 ml of PC; H₂O = 54 ppm
 Agitation Temperature: 35 ± 1°C

Agitation Time, Hrs.	Cu ⁺⁺ Concentration (μg/ml)			
	"Regular" Purity, Code 16*, 0.3% H ₂ O	Low Purity Code 14*, 0.3% H ₂ O	Low Purity, F treated, Code 14-T1* < 0.3% H ₂ O	High Purity Code 1*, < 0.3% H ₂ O
50	400	308	228	---
100	---	---	---	620
200	772	655	597	---
500	867	824	762	811
1000	941	923	885	885

*See Appendix B, page 93, for description

untreated material, and the results are shown in Table XVII. The solubility was reduced by about one-half using DMSO extraction; however, this was not considered an adequate improvement, and no further work with this approach was performed.

TABLE XVII

SOLUBILITY OF DMSO TREATED CuF_2

Electrolyte: 0.05 mols of LiClO_4 in 50 ml P.C.; H_2O = 154 ppm

Temperature: $35 \pm 3^\circ\text{C}$

CuF_2 : Ozark-Mahoning, Low KW-4-105; 0.9% $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$

<u>CuF_2 Treatment</u>	<u>Cu ⁺⁺ Concentration, ($\mu\text{g}/\text{ml}$)</u>		
	<u>1 Week</u>	<u>2 Weeks</u>	<u>3 Weeks</u>
"As Received"	512	543	584
DMSO Extracted	224	256	277

3. 1. 6. Study of Tetraethylammonium Fluoride-Propylene
Carbonate Electrolyte

Since the CuF_2 appears to decompose in the presence of solutes such as LiClO_4 by forming insoluble LiF and moderately soluble $\text{Cu}(\text{ClO}_4)_2$, a CuF_2 -Li cell employing such electrolytes can always be expected to suffer some loss of capacity during open circuit stand. This should not be the case in the presence of electrolytes which allow even a small concentration of fluoride ion in the solution (since the solubility product of CuF_2 should also be very small). Quaternary ammonium fluorides are known to be soluble in organic liquids, and the relatively good conductance of these solutions indicates considerable ionization (although not necessarily fluoride ion activity).

A CuF_2 -Li cell reversible to fluoride rather than lithium ions cannot be built with slab negatives, since these would become passivated by insoluble LiF . However, porous lithium electrodes have been made and tested.³

³McCallum, J.; Simmons, D. E.; and Faust, C. L.; "Investigation of Porous Lithium Battery Electrodes," Technical Report, AFAPL-TR-67-13, (Feb. '67).

The reduction in molar volume upon conversion of Li (13.0 cc/mol) to LiF (9.8 cc/mol) should enhance the efficiency of the electrode. Furthermore, better efficiency could be expected from the CuF_2 electrode in such a cell, since there would be no LiF deposit in the cathode (fluoride ions would be transferred to the anode rather than lithium ions to the cathode). The possibility of building and operating such a cell depends, of course, on the possibility of preparing stable electrolytes having an appreciable fluoride ion activity.

3. 1. 6. 1. Preparation of Solutions

The TEAF obtained from the supplier (Southwestern Analytical Chemicals Co.) contained as much as 25% water, which could not be removed by vacuum drying because of decomposition of the salt as evidenced by a strong amine odor.

For this reason, TEAF-PC solutions were prepared by first recrystallizing the salt from acetonitrile; this procedure alone was found to reduce water content from 15 to 5%. The solution was then made in the desired concentration, and about equal volume of spectroquality benzene was added. The mixture was vacuum distilled overnight, or until removal of benzene was indicated. A molar solution prepared in this manner had a water content (by Karl Fischer) of less than 400 ppm.

3. 1. 6. 2. Conductivity Measurements

Specific conductance measurements for a number of concentrations were obtained and are shown in Table XVIII.

TABLE XVIII

CONDUCTIVITY OF TEAF*-PC SOLUTIONS

Room Temperature (25 - 28°C)

<u>Concentration, mols/1000 ml PC</u>	<u>L_s, mmho/cm</u>
10	9.8
5	12.1
2.5	11.6
1.0	8.3
0.5	4.8

*Water content = 5% (Recrystallized from acetonitrile,
See Section 3. 1. 6. 1.)

The TEAF used for this test had a water content of 5%. The conductivity values obtained compare favorably with those for other solutes in PC; also, the conductivity maximum occurs at a much higher concentration (ca. 5M) than is observed with most other solutes (ca. 1.5M). However, the high water content of these solutions may have affected the results significantly.

3. 1. 6. 3. CuF₂ Solubility Tests

The solubility of CuF₂ (0.9% H₂O) in molar TEAF-PC solution (368 μ g H₂O/ml) was studied at 35°C, and the results obtained are shown in Table XIX. The solubility was below the sensitivity of the iodometric titration (ca. 40 μ g/ml) after 1000 hours of exposure.

TABLE XIX

SOLUBILITY OF CuF₂ IN 1M' TEAF*-PC SOLUTIONS

<u>Time, Hrs.</u>	<u>Cu⁺⁺, (μg/ml)</u>
144	62
336	62
672	<40

*Water content = 368 μ g/ml [Recrystallized from acetonitrile and vacuum distilled (azeotropically)
See Section 3. 1. 6. 1.]

3. 1. 6. 4. Li Stability Test

The visual lithium strip stability test was conducted at 35°C in one molar TEAF-PC solution. The color of the solution over a period of 1000 hours changed from a clear light yellow to a deep yellow. The lithium strip showed little change and was still bright after 1000 hours of exposure.

3. 2. Cell Discharge Tests

Construction of test cells for the low rate portion of the program was similar to that described in Section 2. 3., page 17. For the positive plates, polystyrene binder was used in all tests, and the separation employed in most tests was 0.03 in. thick microporous rubber.

3. 2. 1. Two-Plate Cells With Reference Electrodes

Two-plate cells having reference electrodes immersed directly in the cell electrolyte were designed for studying the discharge characteristics of the negative and positive electrodes. To eliminate electrolyte resistance polarization from potential measurements, the Kordes pulse current load circuit⁴ was used in these tests.

3. 2. 1. 1. Evaluation of Purified Electrolyte Salts

In this test, Li and CuF_2 electrode performance was studied in PC electrolytes containing purified (by recrystallization) and unpurified electrolyte salts. The test cells were constructed as shown in Figure 28, page 68; other construction data are shown in Table XX, page 69. Discharge of the cells began two hours after the addition of electrolyte, and the cell and electrode potential measurements obtained are shown in Figures 29 - 35, page 70 - 76.

The results show, once more, that the reduction of CuF_2 in the PC electrolyte proceeds thru the solution phase, and that its rate at any given potential depends on the solubility of CuF_2 in the electrolyte. In CuF_2 solubility tests, K- and Na- electrolytes give low values of Cu II; consequently, in these electrolytes, the reduction rate obtainable is low. Lithium electrolytes show a high solubility for CuF_2 , and much higher reduction rates can therefore be obtained. The role of the anion, as in the CuF_2 solubility trends, appears to be of secondary importance in the reduction mechanism. Purification of the electrolyte salts by recrystallization improved CuF_2 electrode performance in some cases, but the effect of this variable was comparatively small.

Electrolytes producing low CuF_2 solubility appear to be necessary for wet shelf life. However, a method of "triggering" these cells (*i.e.*, obtaining an initial discharge during which K^+ in the electrolyte would be replaced with Li^+ from the anode reaction) will probably have to be found before these electrolytes can be utilized for appreciable discharge rates.

⁴For a description of test circuit, see S. Abens, et. al., NASA CR-72331, page 22.

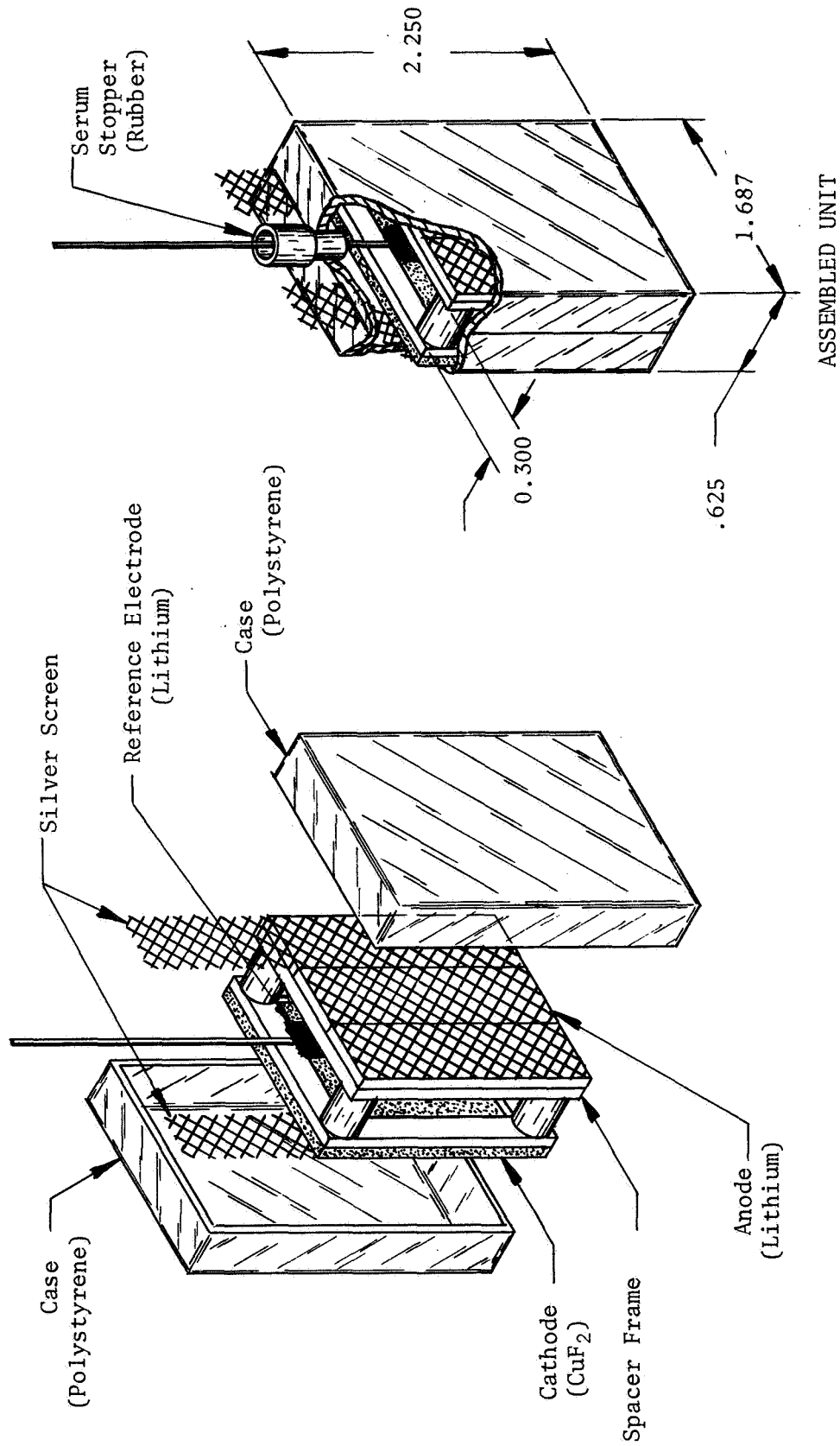


FIGURE 28: TWO-PLATE TEST CELL

TABLE XX

CONSTRUCTION DATA FOR 2-PLATE CuF_2 -Li REFERENCE ELECTRODE CELLS

Propylene Carbonate:	Matheson, Coleman & Bell, distilled from Li powder					
Salts:	LiClO_4 , LiBF_4 , and KAsF_6 (Alfa Inorganic) - vacuum dried 18 hours at 110°C					
CuF_2 :	NaClO_4 , KAsF_6 (Ozark-Mahoning), KPF_6 , NaPF_6 , and KSbF_6 - recrystallized, then vacuum dried 18 hours at 110°C					
Electrolytes:	Ozark-Mahoning, Lot KS-5-95; <0.3% $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, untreated					
Discharge Temperature:	0.05 mols of salt dissolved in 50 ml of propylene carbonate, 20 ml/cell					
Discharge Current:	$35 \pm 2^\circ\text{C}$					
Wet Stand:	7.5 mA (0.5 mA/cm^2)					
	24 Hours at $35 \pm 2^\circ\text{C}$					
Cell No.	Salt	Salt		Recryst.	Electrolyte, H_2O , $\mu\text{g/ml}$	Theo. CuF_2 Cap., AH
		Supplier	Lot #			
1	LiClO_4	GFS	C6	No	54	2.50
2	"	GFS	C6	Yes	76	2.49
3	NaClO_4	GFS	7	No	43	2.21
4	"	GFS	7	Yes	56	2.14
5	KAsF_6	O - M	KW-4-100	No	83	2.84
6	"	Alfa. Inorg.	10-31-6	Yes	40	2.72
7	KPF_6	MC & B	5	No	46	2.58
8	"	MC & B	5	Yes	131	2.57
9	LiBF_4	Footc Min.	63067	No	116	2.52
10	NaPF_6	O - M	KW-4-124	No	59	2.09
11	"	O - M	KW-4-124	Yes	80	1.92
12	KSbF_6	O - M	KW-4-143	No	62	2.32
13	"	O - M	KW-4-143	Yes	76	2.15

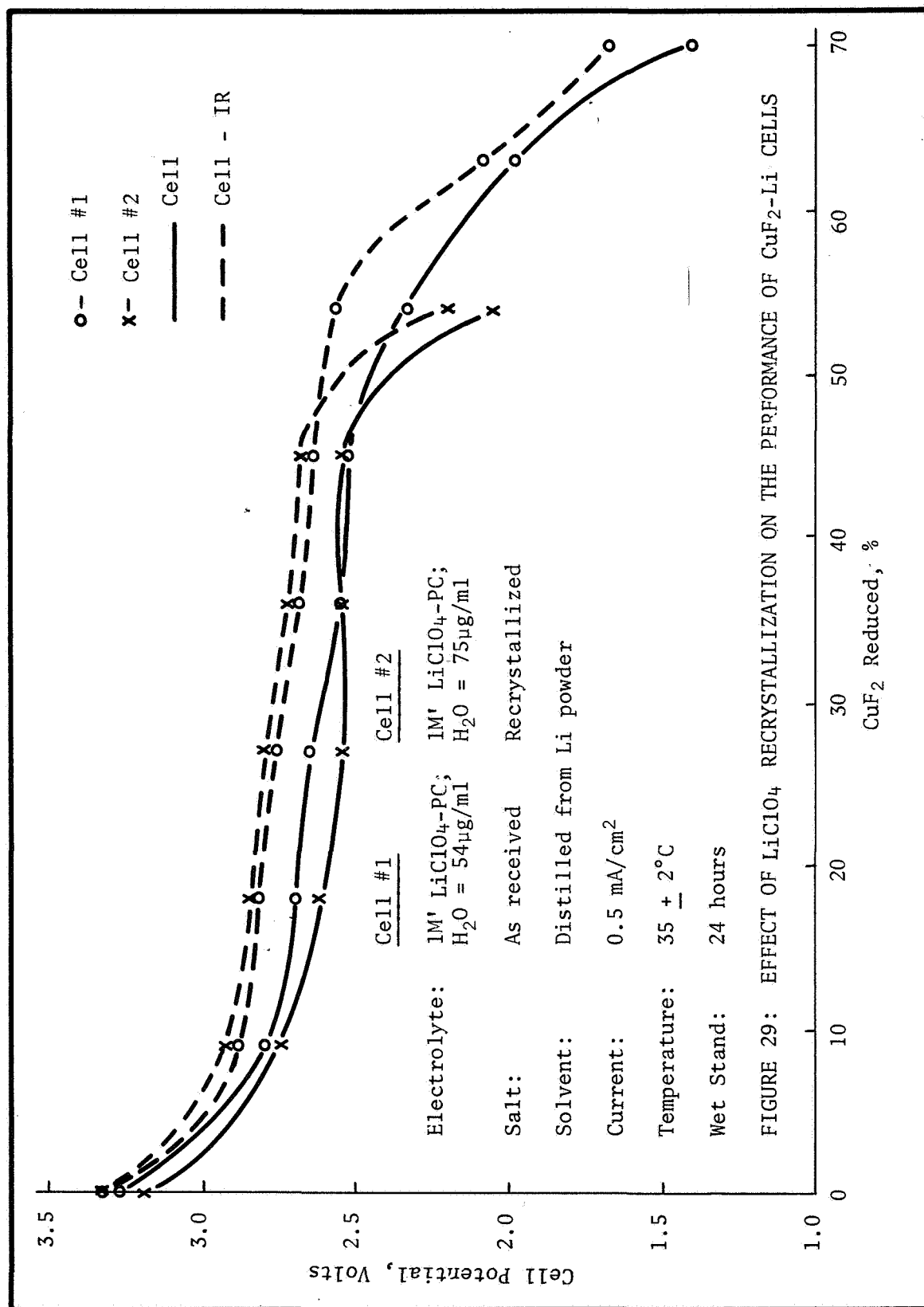


FIGURE 29

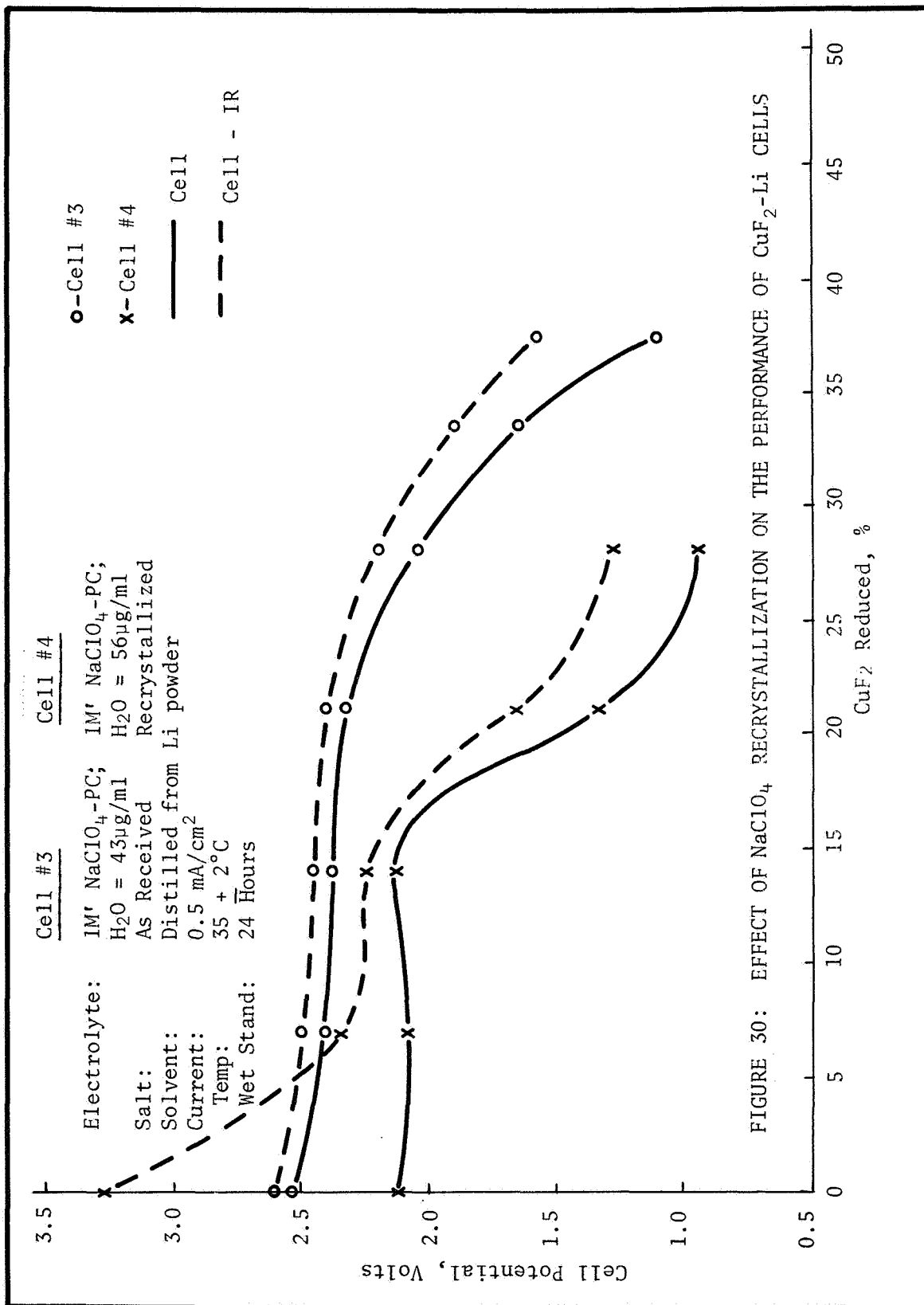
FIGURE 30: EFFECT OF NaClO₄ RECRYSTALLIZATION ON THE PERFORMANCE OF CuF₂-Li CELLS

FIGURE 30

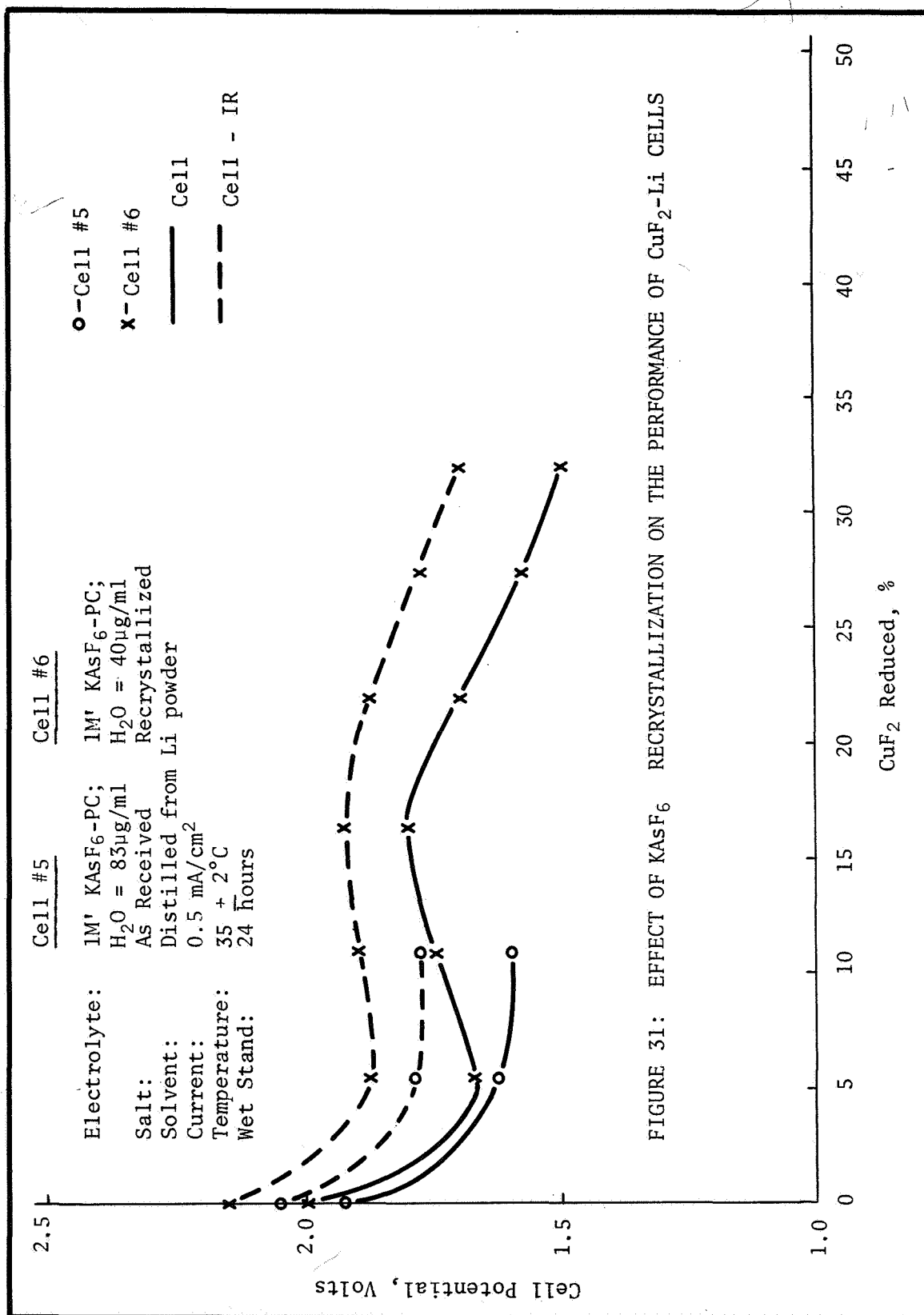
FIGURE 31: EFFECT OF KAsF₆ RECRYSTALLIZATION ON THE PERFORMANCE OF CuF₂-Li CELLS

FIGURE 31.

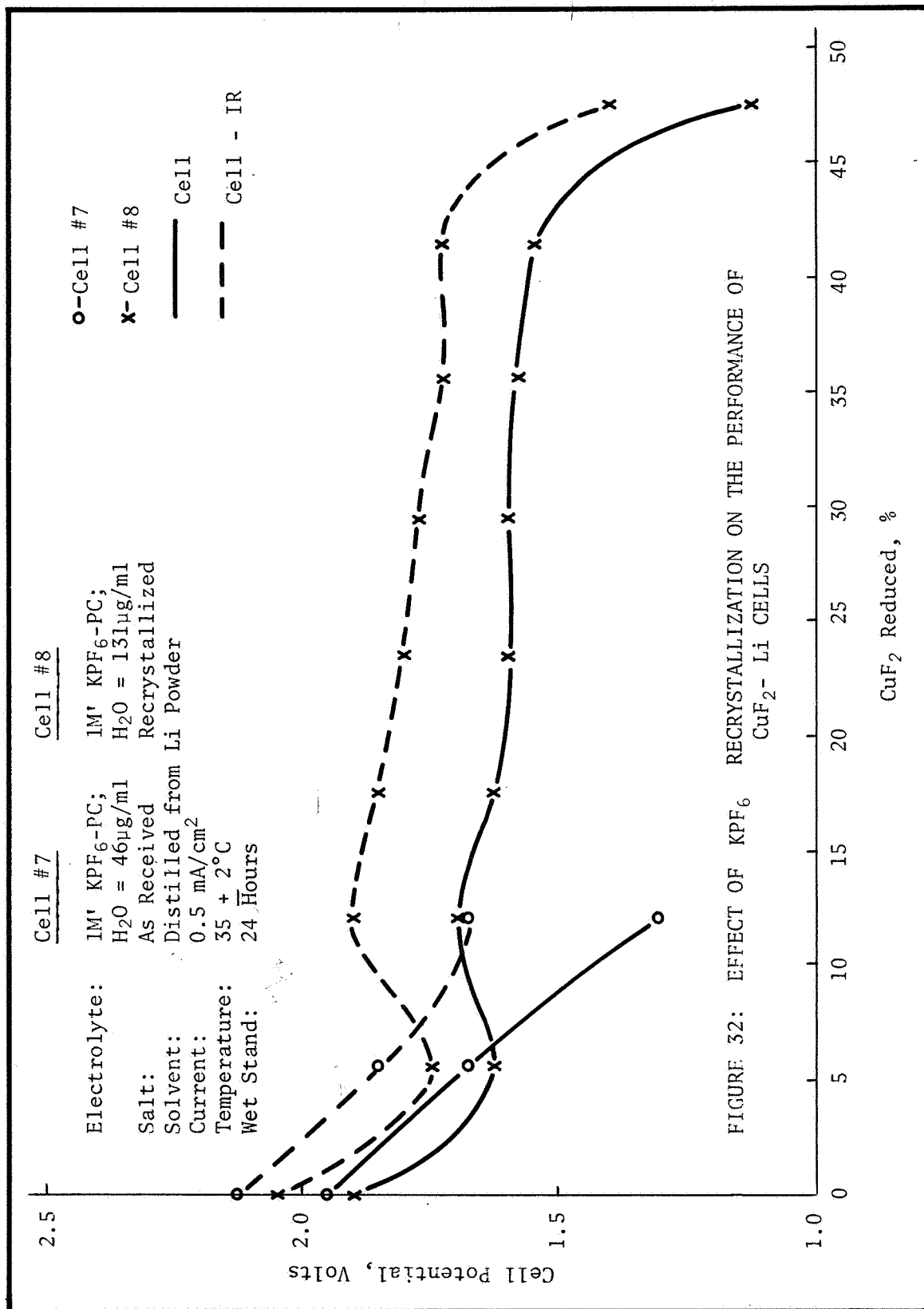


FIGURE 32

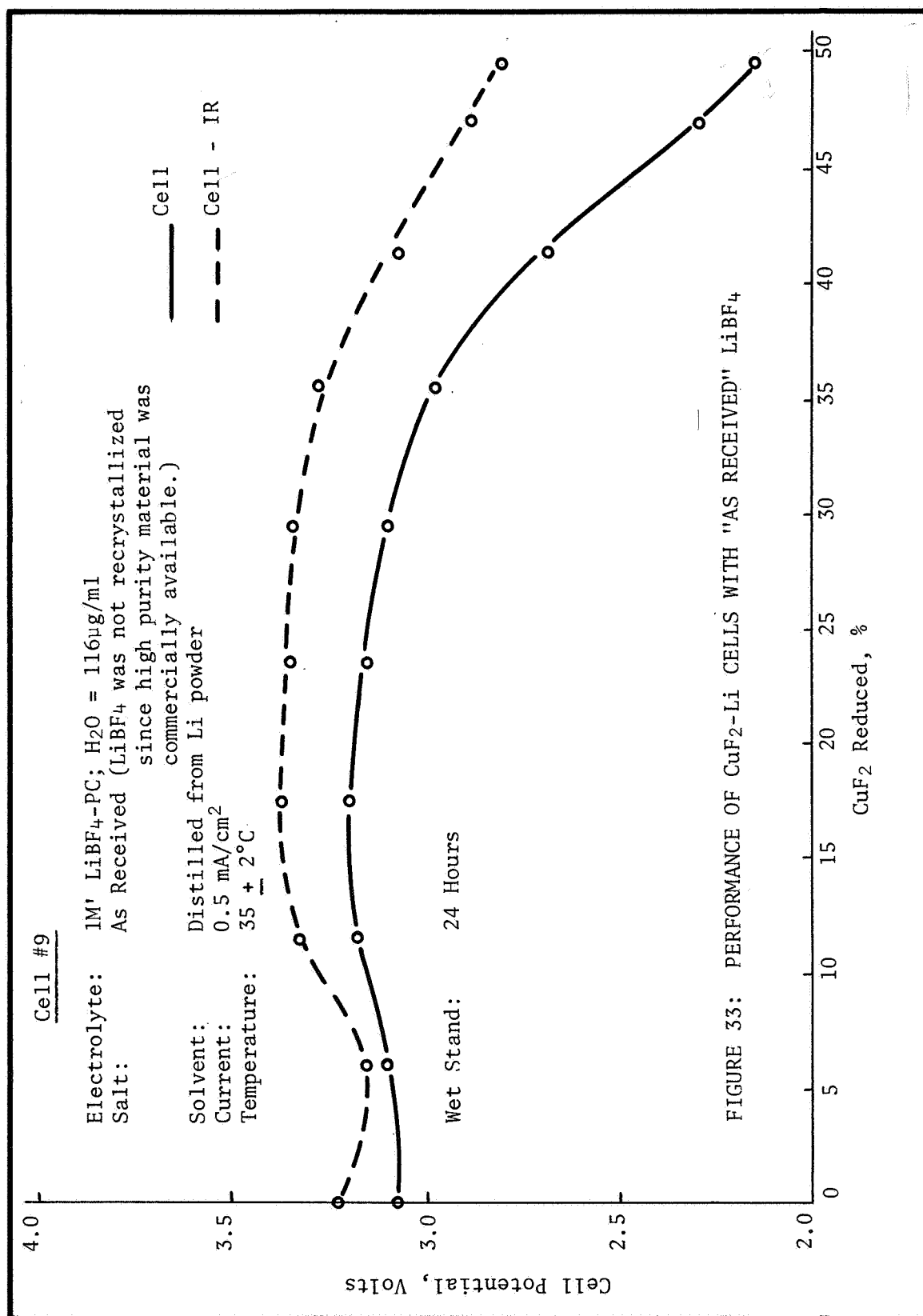


FIGURE 33

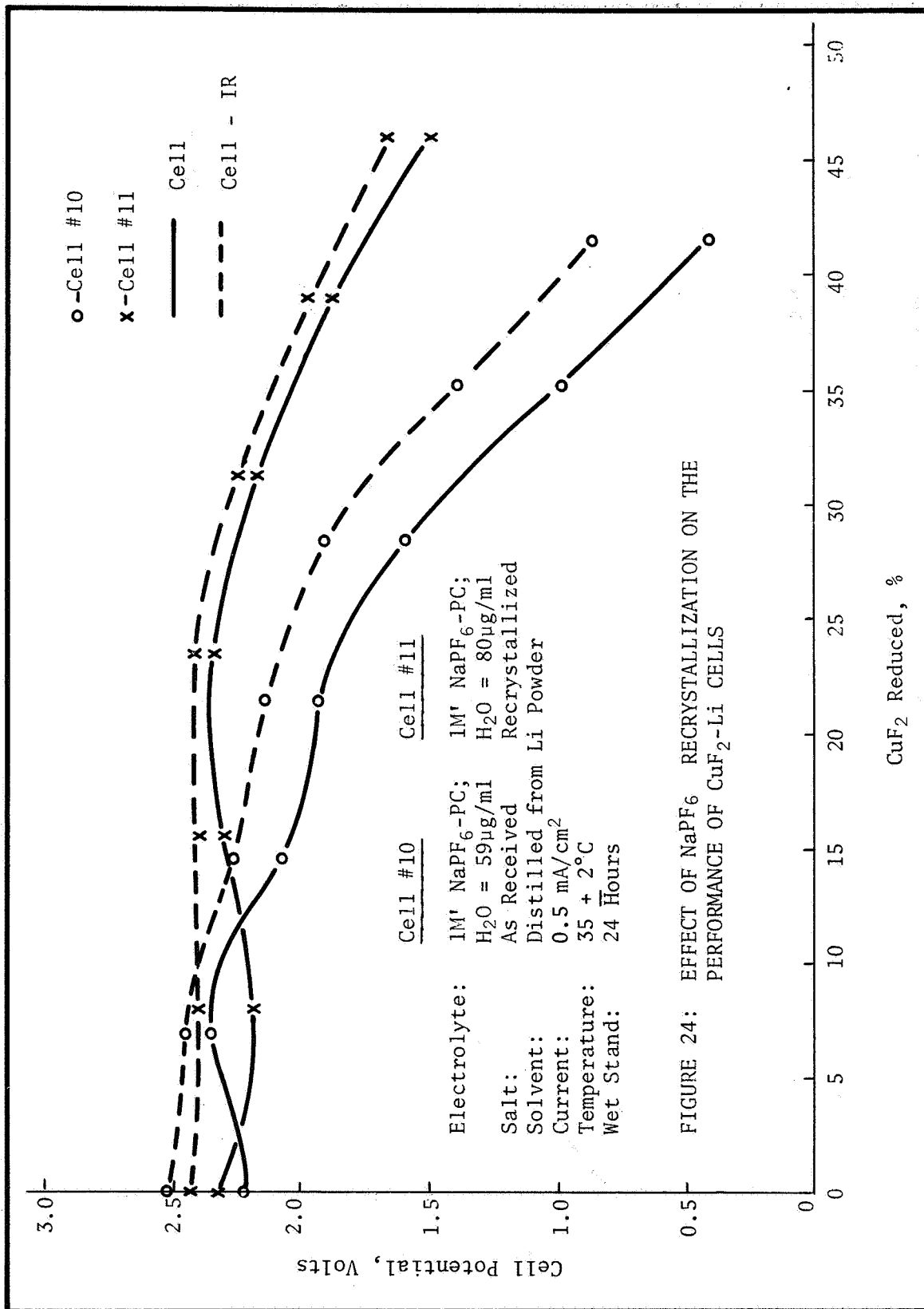
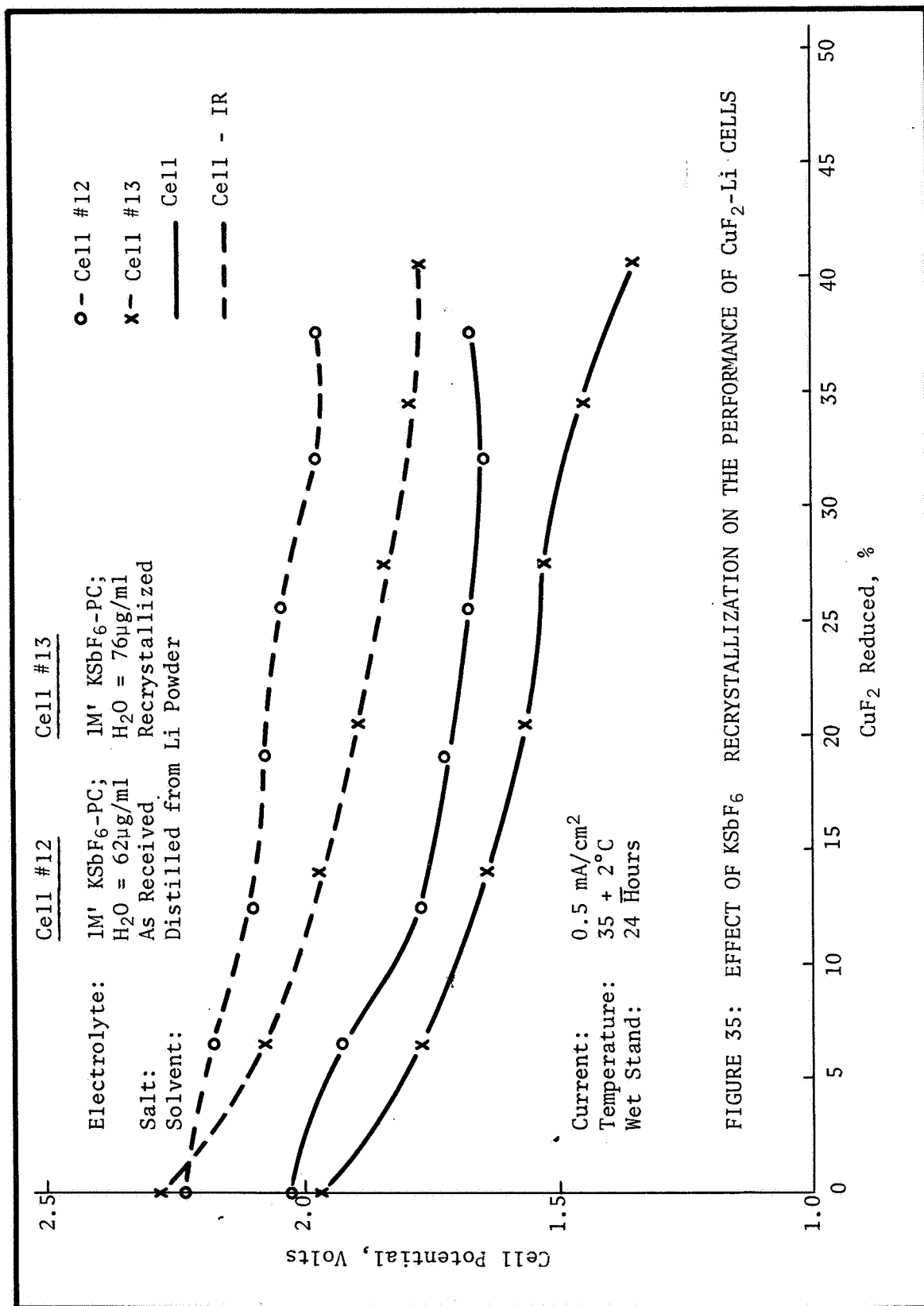


FIGURE 34



3. 2. 1. 2. Reduction of Various Oxidants in KAsF₆-PC Electrolytes

The low discharge rates that are attributed to low CuF₂ solubility in PC electrolytes in the presence of K⁺ ion made it necessary to search for an oxidant that could be added to the CuF₂ cathodes; this oxidant must be capable of reduction at an acceptable rate, until enough Li⁺ ions are present to allow the CuF₂ to solubilize and reduce. It must also be compatible with the CuF₂-Li system in such a way that the wet shelf life of the system is not adversely affected.

The materials selected for this test were MnO₂, AgO, CuF₂, AgCl, and CuF₂·2H₂O; discharges were conducted in 1M KAsF₆/PC electrolyte. For comparison, the reducibility of AgO was also studied in 1M LiBF₄/PC electrolyte. Two-plate cells allowing geometrically unbiased Li reference electrode positioning were constructed between slides in hermetically sealed one inch I.D. compatibility tubes, according to the procedure given in Section 2. 3. 2. 4., page 28. The cells were discharged at 0.5 mA/cm² thru the Kordes pulse current tester.

Results of the discharge tests are summarized in Table XXI, page 78, and cathode potentials vs Li reference electrode are shown in Figure 36, page 79.

Of the materials studied, CuF₂·2H₂O gave by far the most positive reduction potential (after an initial polarization to below 2.0V vs Li). This is a further demonstration for the desirability of having some of this material in the CuF₂ cathode to obtain appreciable discharge rates. Unfortunately, the detrimental effect of CuF₂·2H₂O on wet shelf life in other electrolytes (LiClO₄/PC) will probably preclude its use also in the KAsF₆ electrolyte. In addition, the compatibility tubes containing the CuF₂·2H₂O cathode cells generated up to 60 psig pressures during test (no pressure was obtained for any of the other cells).

Of the other materials, only AgO and AgCl showed somewhat better discharge performance than CuF₂ itself and may, therefore, be useful as an "initiating" additive in Li-CuF₂ cells using a potassium-ion electrolyte such as KAsF₆.

3. 2. 1. 3. Tests With TEAF-PC and TEAF-TMP Electrolytes

Three CuF₂-Li cells were built, activated with 1M¹ TEAF-PC electrolyte (368μg H₂O/ml), and allowed to stand open circuit at 35°C. The OCV of all cells decreased from about 3V initially, to 2.2V in less than 2 hours. Application of 0.5 mA/cm² load caused rapid increase in Li electrode potential, as indicated by CuF₂ reference electrode measurements.

An essentially similar result was obtained with a 1M¹ TEAF-TMP solution. Both results seem to indicate that a blocking LiF film prevents the discharge of the lithium electrode (even though considerable solubility -

TABLE XXI
REDUCTION OF VARIOUS OXIDANTS IN 1M' KAsF₆/PC ELECTROLYTES

Separator: 0.020 inch glass mat							
Load: 0.5 mA/cm ²							
Electrolyte: 1M ⁺ KAsF ₆ /PC (5 ml/cell)							
Temperature: 35 + 1°C							
Cathodes: 24.3g oxidant, 2.44g Conductex SC, 0.25g polystyrene							
Wet Stand: 1 Hour							
Cell No.	Oxidant	OCV	Theo. Cap.	Capacity, 2.5 VF	Capacity, 2.0 VF	Cath. Eff., 2.5 VF	Cath. Eff., 2.0 VF
1	CuF ₂	3.38	.82	.165	.245	20.1	29.9
2	"	3.30	.77	.195	.325	25.2	42.2
3	MnO ₂ *	3.65	1.49	.212	.282	14.2	19.0
4	"	3.75	1.48	.188	.238	12.7	16.2
5	AgO	3.68	.78	.100	.335	12.8	42.8
6	"	3.68	.78	.100	.448	12.8	57.4
7	AgO**	3.84	.74	.075	.110	10.3	14.9
8	"	3.79	.78	.078	.138	9.9	17.7
9	CuF ₂ •2H ₂ O	2.68	.82	.308	.325	37.6	40.0
10	" "	2.95	.81	.225	.225	27.8	27.8
11	AgCl	3.25	.63	.368	.423	58.1	66.7
12	"	3.26	.63	.365	.438	57.7	69.1

* Lavinore B grade

**1M' LiBF₄/PC electrolytes used

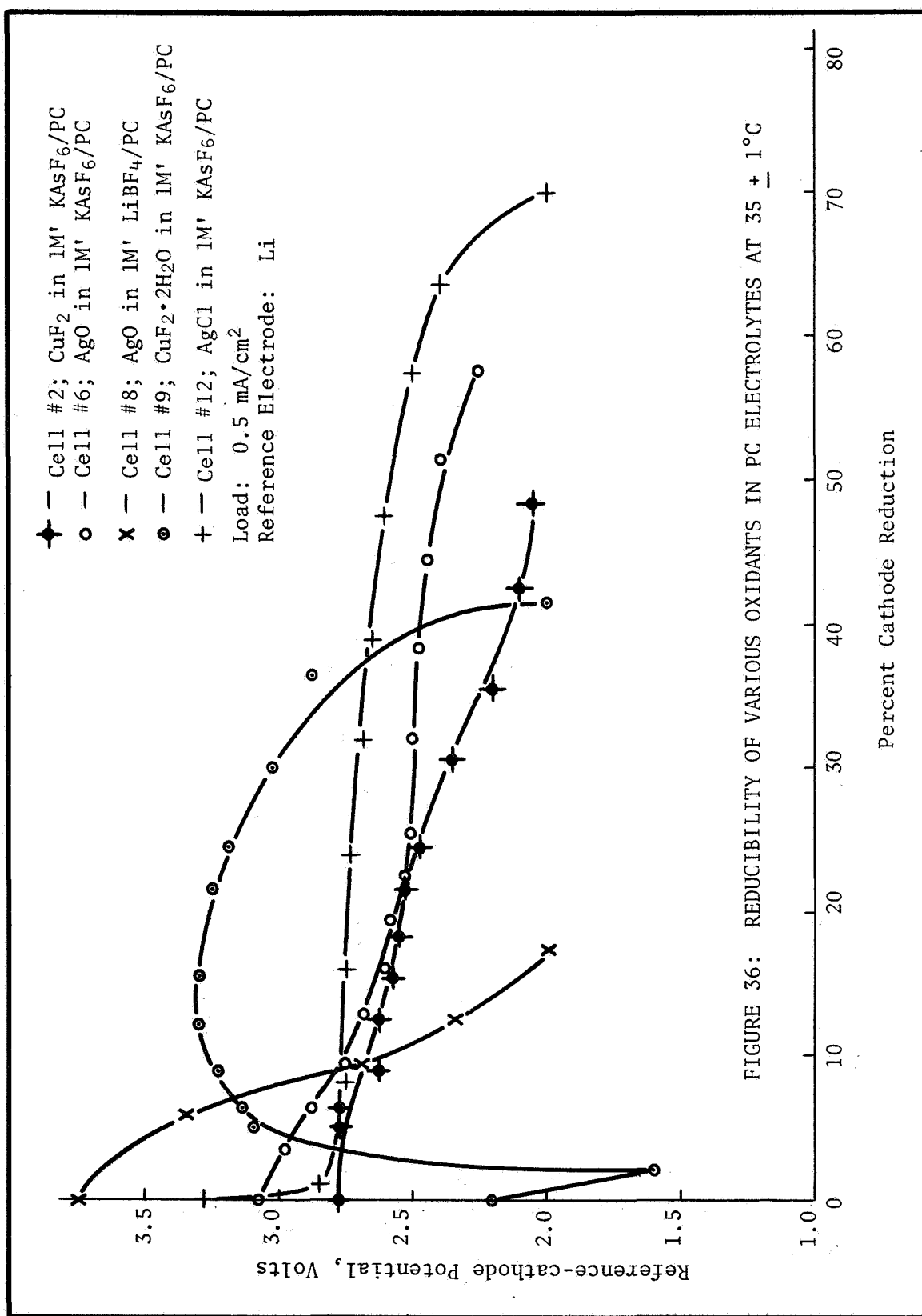


FIGURE 36

up to 15 mols/L - has been observed in this laboratory for LiF in TMP), and that a high surface area electrode structure would be needed for this electrode in a fluoride bearing electrolyte.

3. 2. 2. Three-Plate Cell Tests

Flat-plate cells having two lithium negatives and one CuF_2 positive were built as described in Section 2. 3. 2, page 18, except the cells had more nearly balanced positive and negative capacities (2 - 5 AH positive vs about 9 AH negative). The separation employed for these cells was 0.03 in. thick microporous rubber, and discharges were conducted in hermetically sealed jars at 35°C.

3. 2. 2. 1. Wet Shelf Life With Various Solutes

For this test, the CuF_2 electrodes were prepared by the filter mat technique⁵ and had the composition: CuF_2 - 82%; graphite - 12%; and paper fiber - 6%. The cells were filled with 1M solutions of LiClO_4 , LiBF_4 , KAsF_6 , or NaClO_4 in PC, and they were discharged after 24 or 336 hours of wet stand. Construction and discharge data for these cells are shown in Table XXII, page 81, and Figures 37 - 40, pages 82 - 85.

After 24 hours wet stand, the LiClO_4 -PC cell showed the most efficient CuF_2 reduction efficiency to 2.0VF (58%), while the remaining cells discharged to 40 - 50% of their CuF_2 capacity. After two weeks (336 hours) wet stand, the CuF_2 reduction efficiencies ranged from 8.4 to 19.1%, with KAsF_6 giving the best performance.

Cell #5 polarized after several hours under load, but it subsequently recovered. This phenomenon has been observed in other cells with KAsF_6 electrolyte, and may be due to replacement of potassium ions with lithium ions at the cathode⁶. It is also interesting to note that this polarization had largely disappeared after the two week wet stand period, although discharge performance after the stand was relatively poorer.

⁵For details on this method, see NASA CR-72331, page 134.

⁶In the three-plate cells, the electrochemical equivalent of the electrolyte salt was small (about 0.2AH), compared to that of the cathode (4 - 5 AH in this test).

TABLE XXII

CAPACITY LOSS IN $\text{CuF}_2\text{-Li}$ CELLS IN IM P.C. ELECTROLYTES AT $+35^\circ\text{C}$

Cell	Solute	Stand Time, Hours	Theo. CuF_2 Cap., AH	Hours to 2.0 V	Capacity to 2.0 VF, AH	Average Discharge Potential, Volts	Cathode Eff., %
1	LiClO_4	24	5.17	205	3.01	2.93	58.2
2	"	336	5.04	34	0.42	2.45	8.4
3	NaClO_4	24	4.44	149	2.22	2.97	50.0
4	"	336	4.64	46	0.59	2.57	12.7
5	KAsF_6	96	5.15	165	2.03	2.45	39.4
6	"	336	4.93	79	0.94	2.37	19.1
7	LiBF_4	24	5.04	170	2.52	2.95	50.0
8	"	336	5.03	33	0.43	2.60	8.6

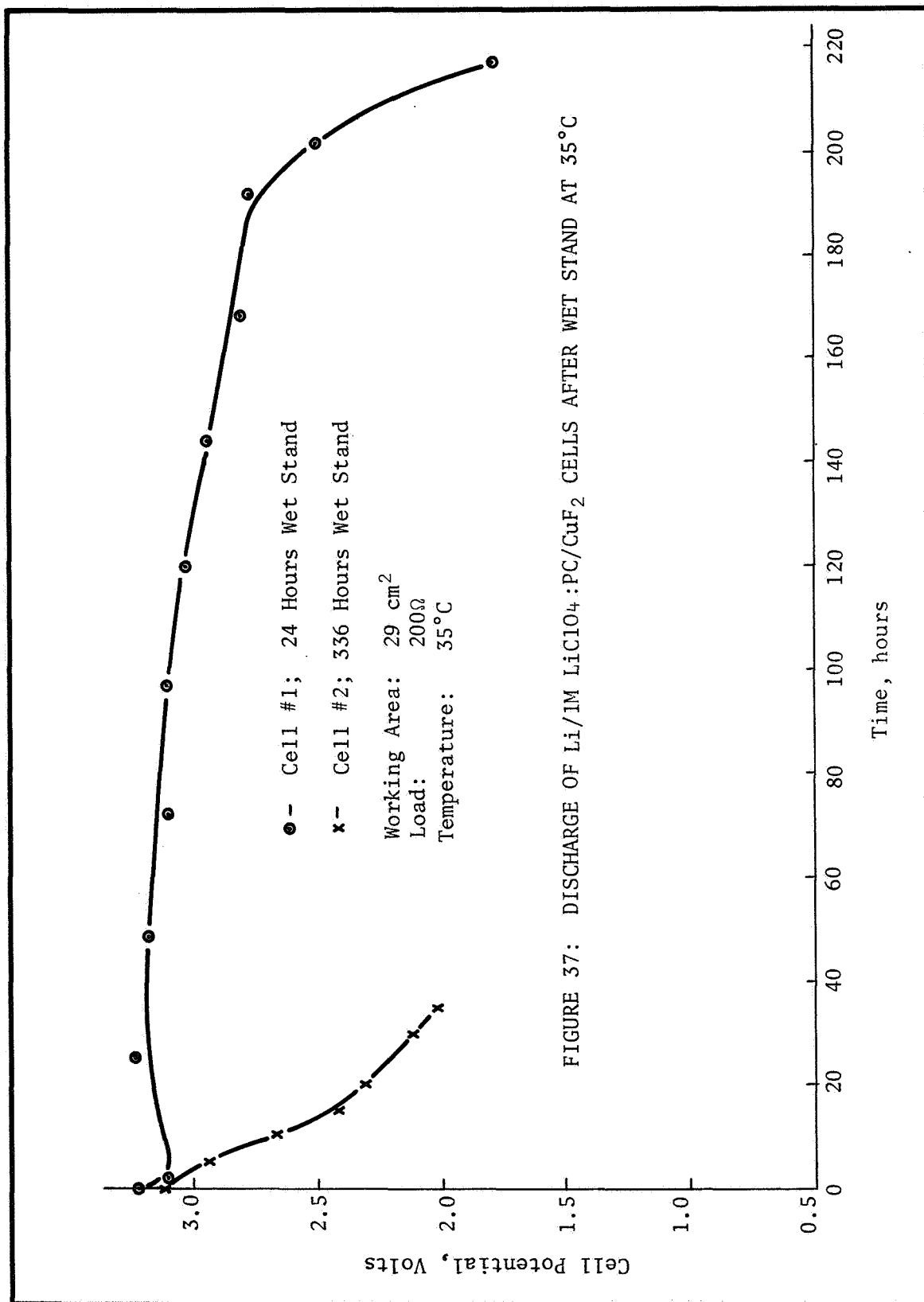


FIGURE 37: DISCHARGE OF Li/1M LiClO₄:PC/CuF₂ CELLS AFTER WET STAND AT 35°C

FIGURE 37

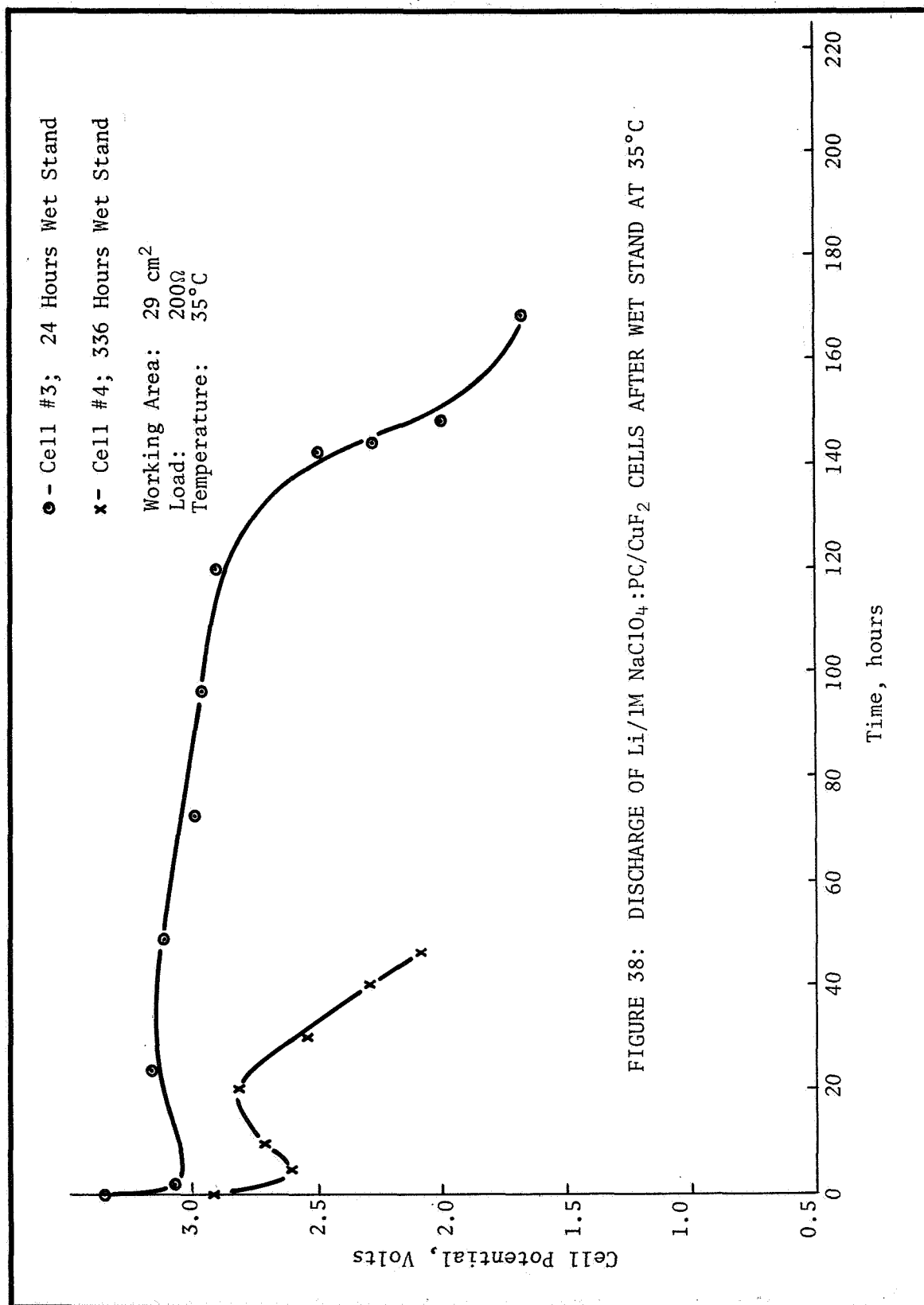


FIGURE 38

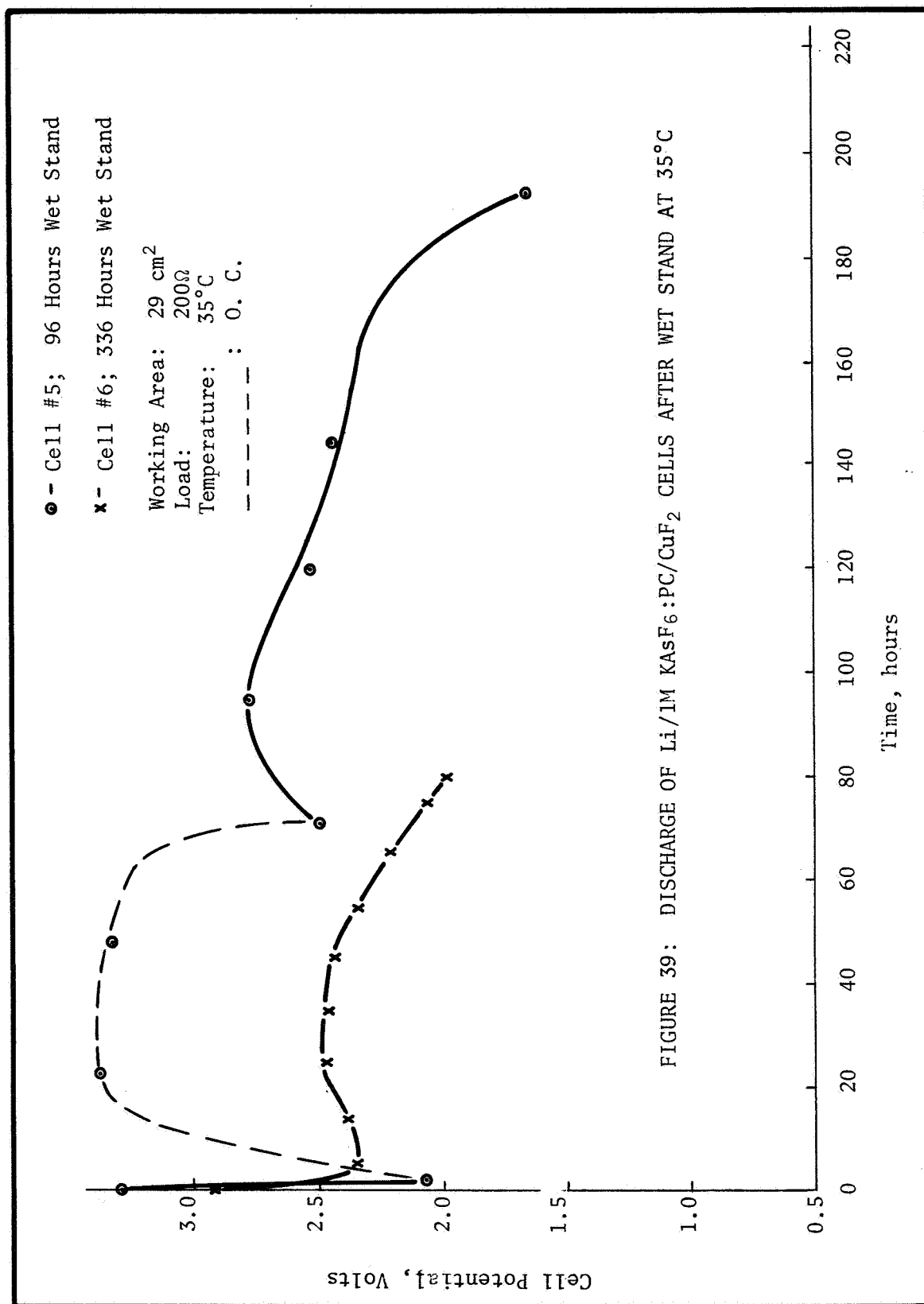


FIGURE 39

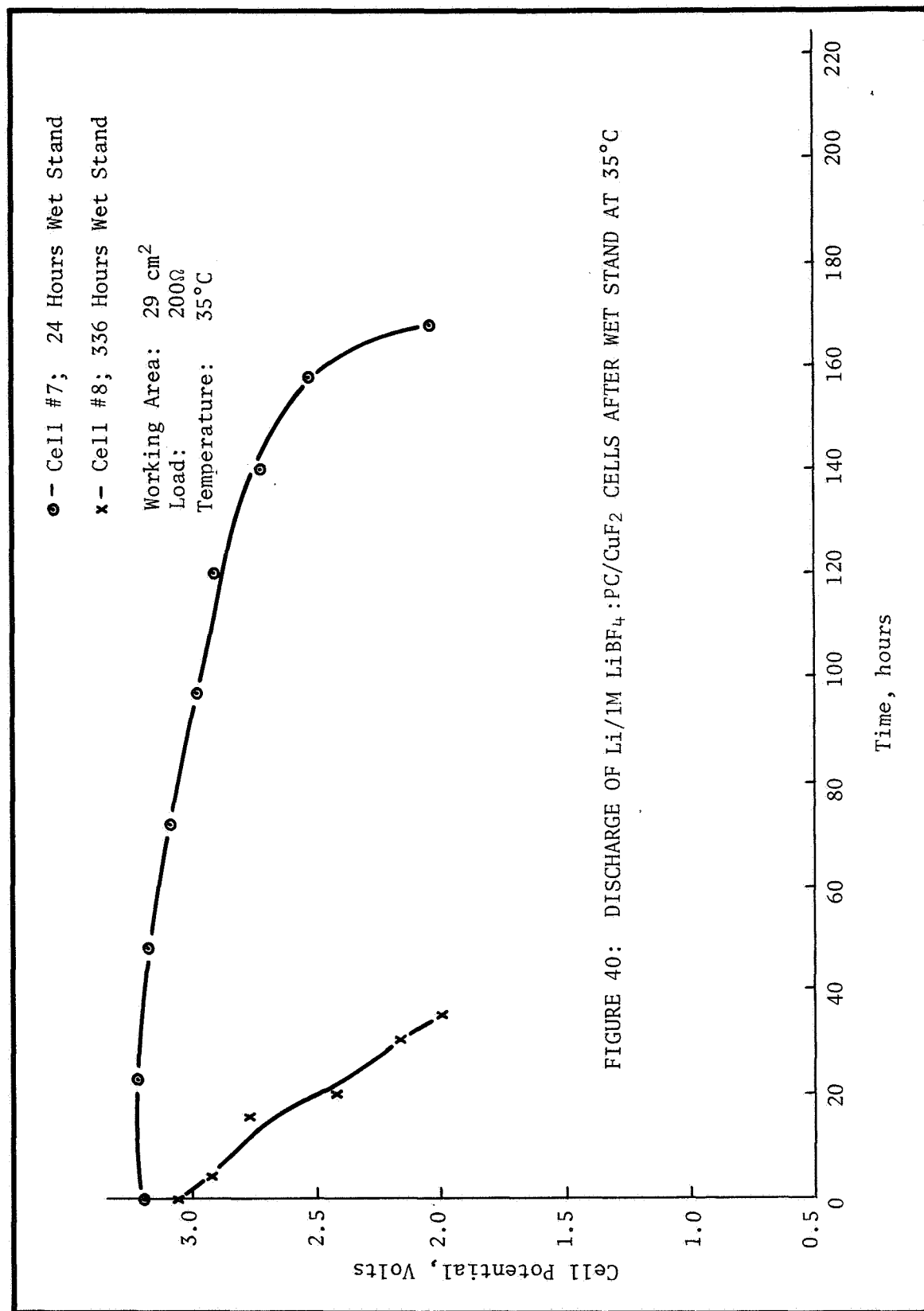


FIGURE 40

3. 2. 2. 2. Performance of CuF_2 From Various Sources

The purpose of these tests was to evaluate performance of cells built with CuF_2 from various sources having various purity levels. The materials used were those described in Section 3. 1. 4, page 57, and the positive electrodes had the composition: CuF_2 - 100, Conductex SC - 10, and polystyrene - 2. The cells, with 1M LiBF_4 -PC, were discharged thru 200 Ω loads after wet stand periods of 24 and 336 hours at 35°C. Construction and summarized discharge data for these cells are shown in Table XXIII, page 87, and voltage-time data for the discharges are plotted in Figures 41 - 44, pages 88 - 91.

After 24 hours of wet stand, the best cell with each type of CuF_2 gave about 60% cathode efficiency to 2.0VF; however, considerably lower discharge potentials were obtained with the F_2 -treated CuF_2 than with the other materials. Those cells having fluorine treated or "high purity" CuF_2 showed significantly better capacity retention after two weeks of wet stand at 35°C. These results show that both low water content and high purity are conducive to improved wet stand capability in these cells; however, this is to a large degree achieved at the expense of the discharge rate capability of the system. Therefore, it again appears that, with the present technology, the cells would have to be "tailored" for each application; i.e., a very low water content and high purity CuF_2 would have to be used where some wet stand and only low discharge rates are required, and a somewhat higher water content would be required in cells for higher rate applications. This situation has also been studied and found to be similar in the case of the high rate (methyl formate) CuF_2 -Li system, where water is added to the cathode in the form of $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ to obtain the desired discharge rates.

TABLE XXIII

WET STAND PERFORMANCE OF CELLS CONTAINING CuF_2 FROM VARIOUS SOURCES

Load:	200Ω (≈0.5 mA/cm ²)						
Electrolyte:	1M ⁺ LiBF ₄ /PC; H ₂ O = 133μg/ml						
Temperature:	35 + 1°C						
Cathodes:	89% ⁻ CuF ₂ , 9% Conductex SC, 2% polystyrene						
Cell No.	CuF ₂ Code*	Theo. CuF ₂ Cap., AH	Stand Time, Hours	Capacity to 2.0V	Time to 2.0V, Hours	Average Potential to 2.0V	Efficiency to 2.0V, %
1	14	2.57	336	0.24	25	2.05	9.9
2	14	2.56	336	0.35	29	1.99	11.3
3	14	2.47	24	1.48	96	3.08	59.9
4	14	3.09	24	1.28	83	3.08	41.4
5	14-T2	2.36	24	1.28	100	2.56	54.3
6	14-T2	2.43	24	1.59	123	2.58	65.3
7	14-T2	2.49	336	0.97	75	2.58	38.9
8	14-T2	2.32	336	0.91	75	2.43	39.4
9	16	2.94	24	1.76	116	3.04	60.0
10	16	2.69	24	1.60	105	3.04	59.3
11	16	2.68	336	0.68	51	2.68	25.5
12	16	2.49	336	0.28	23	2.40	11.1
13	1	2.59	24	1.61	104	3.07	62.0
14	1	2.98	24	1.44	99	2.90	48.2
15	1	2.54	336	0.79	63	2.50	31.0
16	1	2.50	336	1.08	80	2.70	43.3

*See Appendix B, page 93, for description.

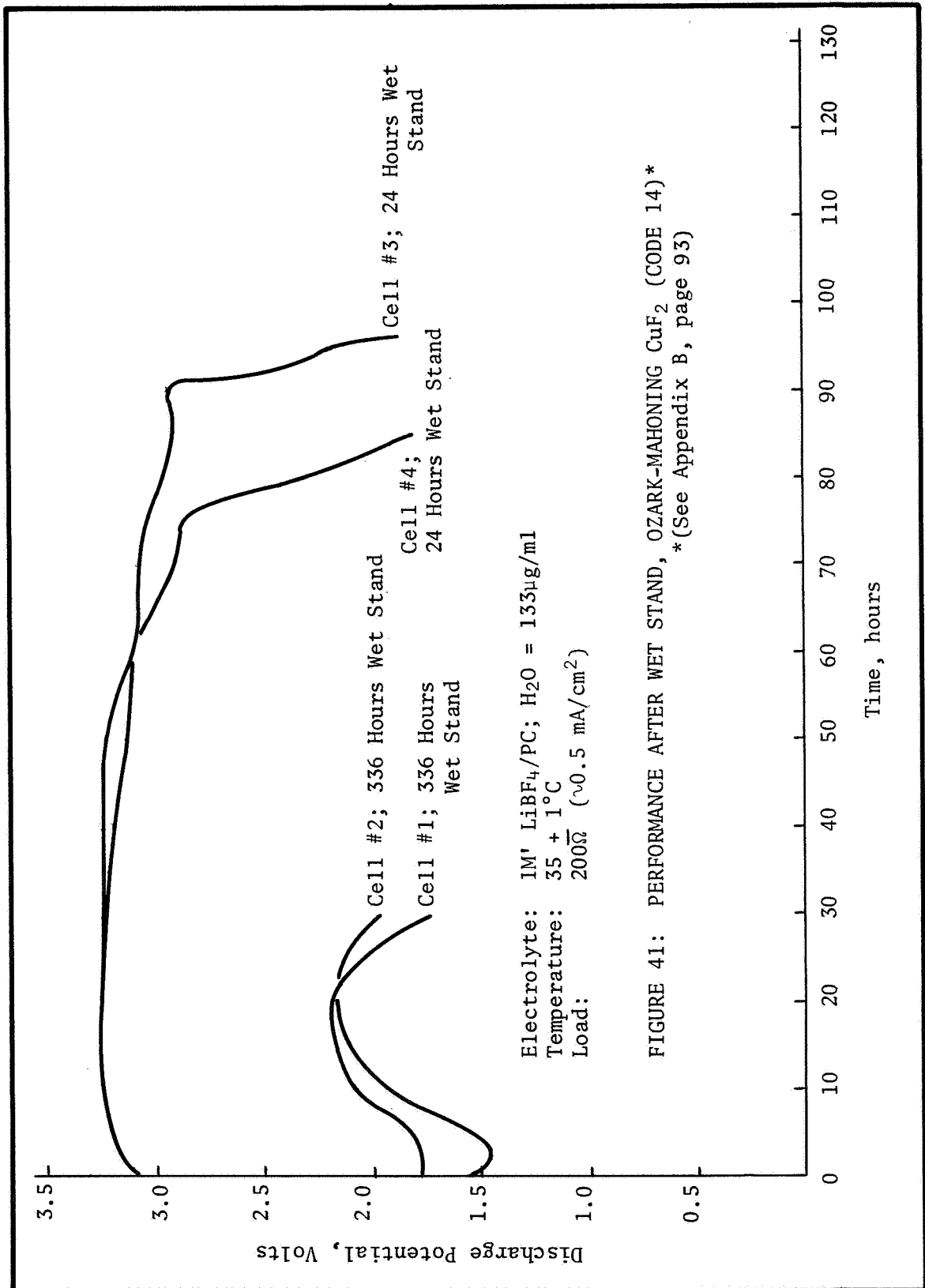


FIGURE 41

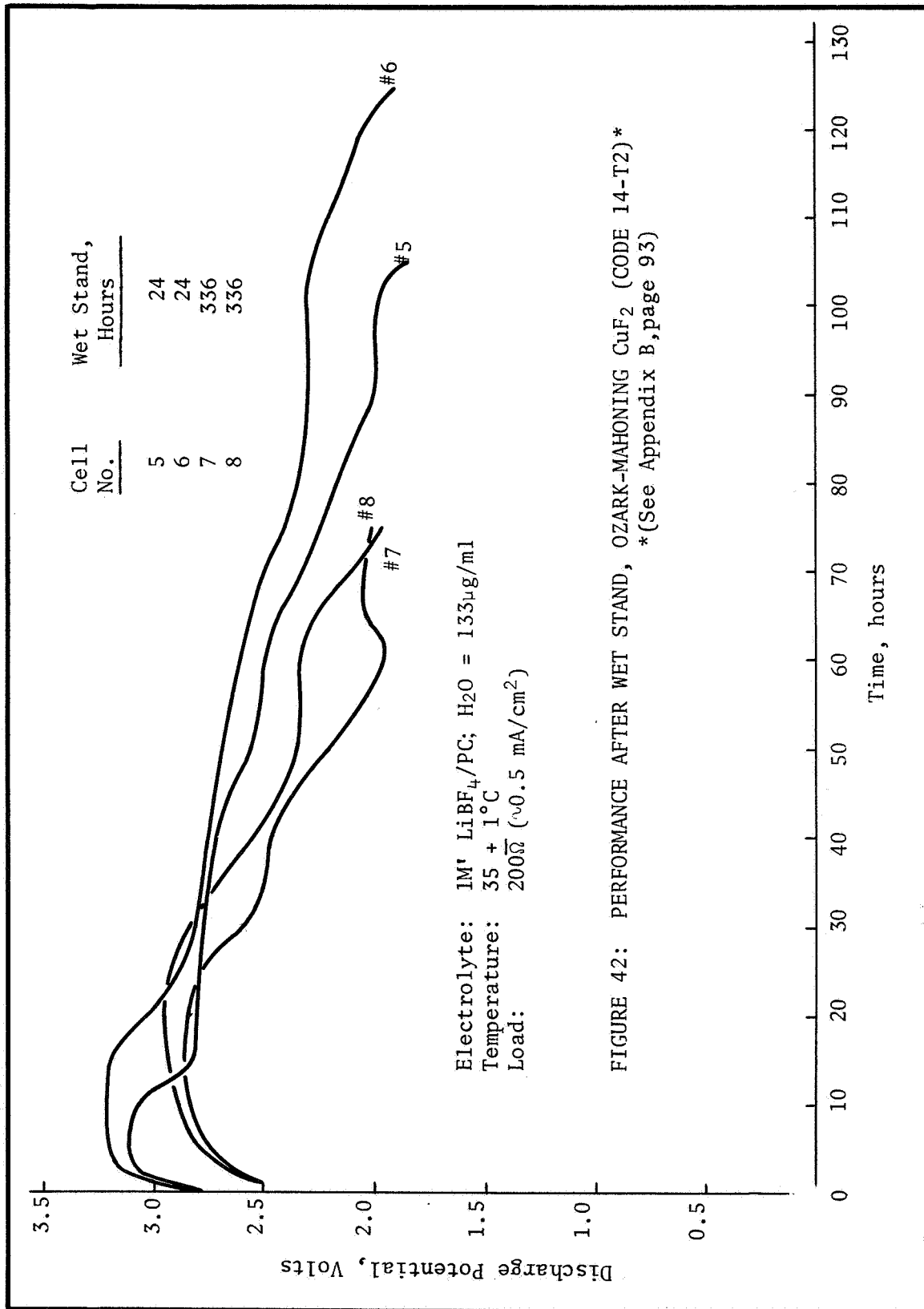


FIGURE 42

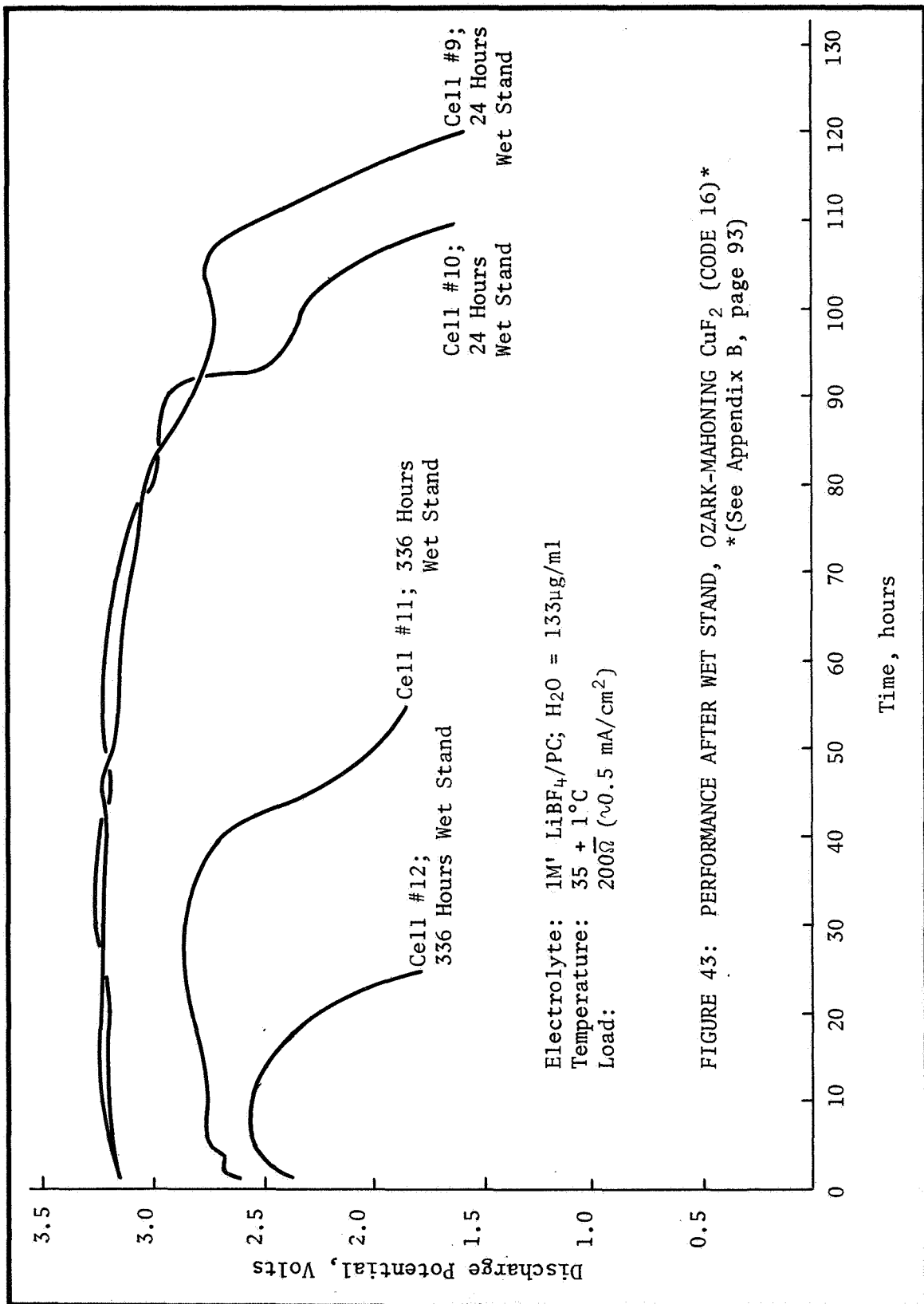


FIGURE 43

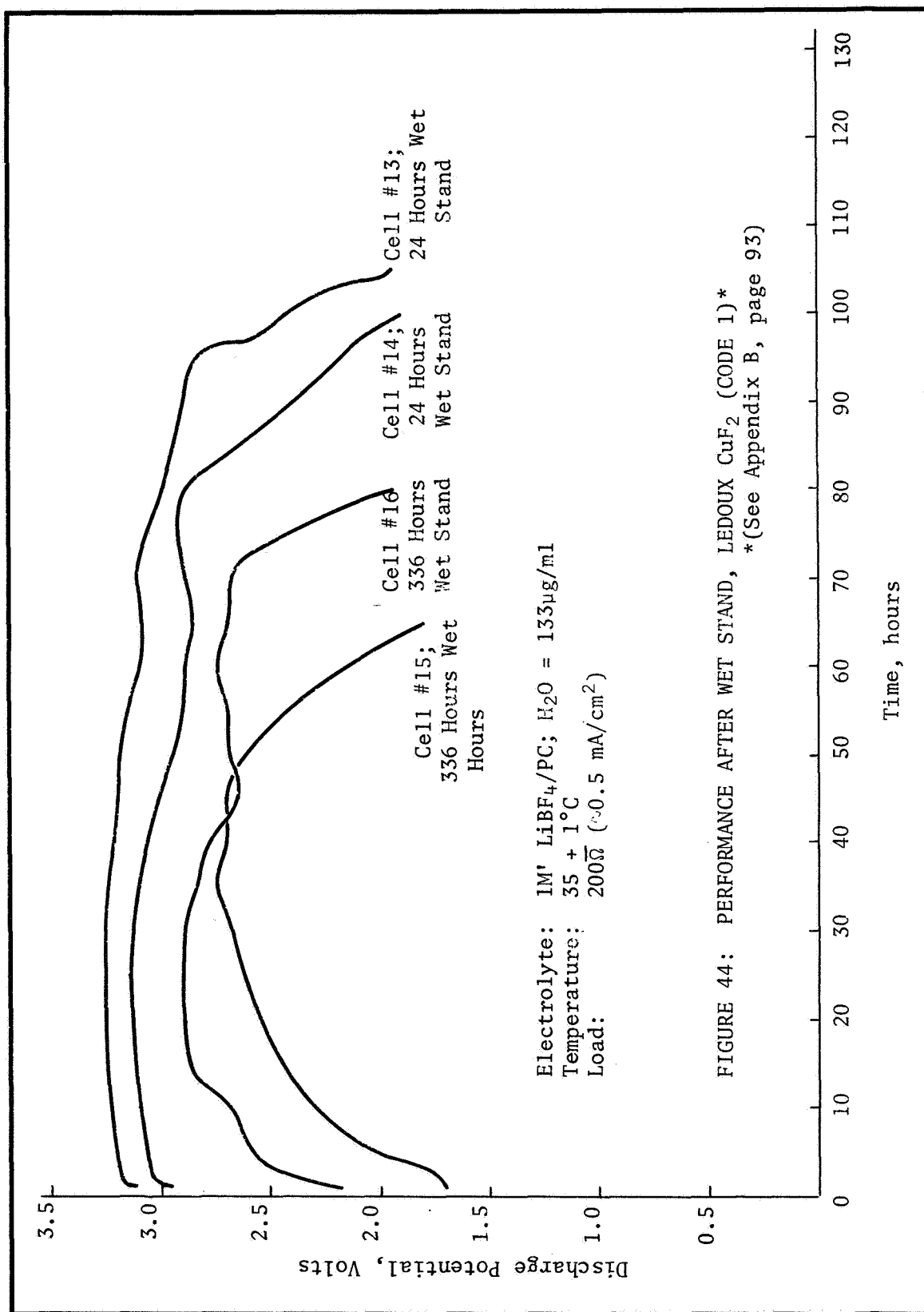


FIGURE 44: PERFORMANCE AFTER WET STAND, LEDOUX CuF₂ (CODE 1)*
 *(See Appendix B, page 93)

FIGURE 44

4. APPENDIX A - PURIFICATION OF SPECTROQUALITY METHYL FORMATE

Methyl formate purification was performed according to the following procedure:

1. A glass wool plug is inserted into one end of an 18 in. long x 1 1/16 in. diameter column, and the column is filled with 70 grams of new or freshly regenerated Linde 4A Molecular Sieve 1/16 in. pellets.
2. The column is then attached to one neck of a three-neck distillation pot with a stop-cock in between. The top of the column is closed off and, with a Vigreux Column, condenser, and receiver in place, a hard vacuum is applied to the entire apparatus for 16 hours.
3. After 16 hours, the apparatus is back filled with dry air, and a separatory funnel containing the methyl formate is attached to the top of the sieve column. The MF is then passed through the column into the pot at the rate of 26 ml/min.
4. After the effluent methyl formate is collected in the pot, the stop-cock between the column and the pot is closed. Lithium powder is then quickly added to the methyl formate in the pot (1g Li/1000 ml MF), and the solution is agitated for 30 minutes.
5. Distillation then takes place at atmospheric pressure. Both the initial and final 10% of the distillate is rejected, and the 80% center cut is collected.
6. The 80% fraction of the methyl formate is transferred to the pre-dried serum bottles and hermetically sealed. It is assayed for water content by the Karl Fischer method. Batches which have a water content above 200 μ g/ml are rejected.

5. APPENDIX B - MATERIALS LIST

5. 1. CuF₂ Materials ListCuF₂ MATERIALS LIST

<u>Material</u>	<u>LEL Code</u>	<u>Supplier</u>	<u>Cat. No.</u>	<u>Description</u>	<u>Treatment</u>	<u>% H₂O by X-Ray Anal.</u>
CuF ₂	13-1	Ozark	S-66	Lot KW-41-105	None	0.3
"	13-2	"	"	"	"	"
"	13-3	"	"	"	"	"
"	13-4	"	"	"	"	"
"	13-5	"	"	"	"	"
CuF ₂	14	"	"	Lot PS-1-12D	None	0.5
"	14-T1	"	"	"	Fluorine	<0.3
"	14-T2	"	"	"	"	<0.3
CuF ₂	15	"	"	Lot KW-5-38	None	<0.3
CuF ₂	16	"	"	Lot KW-5-95	"	<0.3
CuF ₂	17	"	"	Lot R-6-134	"	---
CuF ₂	19	"	"	Lot KS-5-102B	"	---
CuF ₂	20	"	"	Lot KS-5-128	"	<0.3
CuF ₂	21	"	"	Lot RT-5-14	"	<0.3
CuF ₂	1	Ledoux	----	----	"	0.56
CuF ₂ •2H ₂ O	5	Ozark	S-71	Lot KW-4-54, 99% min.	"	>26.0

5. 2. Electrolyte Salts Materials List

ELECTROLYTE SALTS MATERIALS LIST

<u>Material</u>	<u>LEL Code</u>	<u>Supplier</u>	<u>Cat. No.</u>	<u>Description</u>	<u>Treatment</u>
LiClO ₄	2	Smith	----	Lot B-7	Dried @ 150°C vac.
NaClO ₄	2	"	----	Lot 7	" " " "
KAsF ₆	2	Ozark	S-206	Lot KW-4-100, 98% min.	" " " "
LiBF ₄	2	Foote	----	99% min.	" " " "
NaAsF ₆	2	Alfa	----	Lot As-106, 99% min.	" " " "
NaClO ₄	3	Smith	----	Lot 7,99% min.	Dried @ 110°C vac.
KAsF ₆	3	Alfa	AS-105	Lot 10-3-6, 99% min.	" " " "
KAsF ₆	3	Ozark	S-206	Lot KW-4-100, 98% min.	" " " "
NaAsF ₆	3	"	S-566	Lot KW-4-123, Custom made	" " " "
LiBF ₄	3	Foote	----	98% min.	" " " "
KSbF ₆	3	Ozark	S-511	Custom made	" " " "
LiPF ₆	3	"	S-121	Lot R-6-88, 97% min.	None
LiClO ₄	3	Smith	----	Lot B-7	Dried @ 110°C vac.
NaPF ₆	3	Ozark	S-246	Lot KW-4-124, 98% min.	" " " "
KPF ₆	3	Matheson	PX1475	Lot 5	" " " "

ELECTROLYTE SALTS MATERIALS LIST (Continued)

<u>Material</u>	<u>LEL Code</u>	<u>Supplier</u>	<u>Cat. No.</u>	<u>Description</u>	<u>Treatment</u>
NaClO ₄	3R	Smith	---	Lot 7	Recrystallized - dried @ 110°C vac.
KAsF ₆	3R	Ozark	S-206	Lot KW-4-100	" " " "
KSbF ₆	3R	"	S-511	Lot KW-1-143	" " " "
LiClO ₄	3R	Smith	----	Lot B-7	" " " "
NaPF ₆	3R	Ozark	S-246	Lot KW-4-124	" " " "
KPF ₆	3R	Matheson	PX1475	Lot 5	" " " "
TEAF	1	Southwest	----	----	None
TEAF	1R	"	----	----	Recrystallized

5. 3. Electrolyte Solvents Materials List

<u>ELECTROLYTE SOLVENTS MATERIALS LIST</u>					
<u>Material</u>	<u>LEL Code</u>	<u>Supplier</u>	<u>Cat. No.</u>	<u>Description</u>	<u>Treatment</u>
Propylene Carbonate	2	Matheson	PX 1705	Lot 14 Spectroquality	Lithium & dist.
Trimethyl Phosphate	5	"	TX 1429	Lot 10 Practical	Distillation
Diglyme	5	"	-----	Lot 9 Spectroquality	Dist. from LiAlH ₄
Glyme	5	"	DX 1530	Lot 22 Spectroquality	Dist. from LiAlH ₄
Propylene Carbonate	6	"	PX 1705	Spectroquality	None
Dimethyl Formamide	6	"	DX 1730	Lot A-49 Spectroquality	None
Dimethyl Sulfoxide	6	"	MX 1457	Lot 15 Spectroquality	None
Propylene Carbonate	8	"	PX 1705	Spectroquality	Dist. from Li powder
Methyl Formate	1	"	MX 1040	Spectroquality	None
N-nitroso-dimethylamine	1	Eastman	7370	-----	-----
Acetonitrile	1	Matheson	AX 145	Spectroquality	-----

5. 4. General Materials List

<u>GENERAL MATERIALS LIST</u>			
<u>Material</u>	<u>Supplier</u>	<u>Cat. No.</u>	<u>Description</u>
Na ₂ S ₂ O ₃	Hellige	R 1231C	0.1 N
Karl Fischer Reagent	Harleco	3786	Stabilized Sol'n
Karl Fischer Reagent	Fisher	SO-K-3	----
Karl Fischer Water Std.	Harleco	1849	----
Karl Fischer Water Std.	Fisher	SO-W-2	----
KI	Baker	3164	Reagent
Acetic Acid	Fisher	A-38	"
Ethyl Acetate	Baker	9280	"
Xylene	Matheson	CB 821	"
Molecular Sieve	Linde	1/16" pellets	4A
Acetone	Matheson	AX 120	Reagent
LiAlH ₄	Metal Hydrides	----	----
Lithium Ribbon	Footc	----	1/2 x 1/16 in.
Lithium Metal Ribbon	"	----	2 x .015 in.
Lithium Metal Powder	"	----	98.5% Li
Graphite	Dixon	----	Air-Spun Graphite
Carbon Black	Columbian	----	Conductex SC

GENERAL MATERIALS LIST (Continued)

<u>Material</u>	<u>Supplier</u>	<u>Cat. No.</u>	<u>Description</u>
Cellulose Acetate	Eastman	4644	ASTM Visc. 3
Microporous Rubber	American	-----	0.030 in.
Glass Mat	Reeve Angel	934-AH	-----
Silver Grid	Ex-Met	-----	5 Ag 14-1/0
Silver Grid	Ex-Met	-----	5 Ag 8-1/0
Ethyl Ether	Matheson	-----	-----
Heptane	"	HX 77	Spectroquality
Petroleum Ether	"	PX 425	Reagent
Stannic Chloride	Baker	9434	"
Phosphorous Pentoxide	Merck	7143	"
Sodium Carbonate	Fisher	S-263	"
P-Dioxane	Matheson	PX 2095	Spectroquality
Ethanol	Publicker	-----	Lot 12567 - Absolute
Methanol	Matheson	MX 475	Spectroquality
AgO	City	-----	-----
AgCl	"	-----	-----
MnO ₂	Lavinore	-----	-----

6. APPENDIX C - LIST OF SUPPLIERS

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Beverly, Mass.

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Butler, N. J.

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North Broad Street
Phillipsburg, N. J.

City Chemical Corp.
130 West 22nd Street
New York, N. Y.

Columbian Carbon Co.
250 Kings Highway East
Haddonfield, N. J.

Joseph Dixon Crucible Co.
Division 48-C
Jersey City, N. J.

Eastman Organic Chemical
Products, Inc.
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Framingham, Mass.

Exmet Corp.
123 Marbledale Road
Tuckahoe, N. Y.

Fisher Scientific Co.
Gulph Road (Route 23)
King of Prussian, Pa.

Foote Mineral Co.
Route 100
Exton, Pa.

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(HARLECO)
60th & Woodland Ave.
Philadelphia, Pa.

Hellige, Inc.
877 Stewart Avenue
Garden City, N. Y.

E. J. Lavino & Co.
Philadelphia, Pa.

Ledoux & Co., Inc.
359 Alfred Avenue
Teaneck, N. J.

Linde Division, Union Carbide Corp.
270 Park Avenue
New York, N. Y.

Matheson, Coleman & Bell
Jackson & Swanson Streets
Philadelphia, Pa.

Merck & Co., Inc.
1935 Lincoln Avenue
Rahway, N. J.

Metal Hydrides
Beverly, Mass.

Ozark-Mahoning Co.
310 West Sixth
Tulsa, Okla.

Publicker Industries, Inc.
1429 Walnut Street
Philadelphia, Pa.

H. Reeve Angel & Co., Inc.
9 Budewell Place
Clifton, N. J.

George B. Smith Chemical Works, Inc.
1 Center Street
Maple Park, Ill.

Southwestern Analytical Chemicals, Inc.
821 East Woodward
Austin, Tex.

7. APPENDIX D - PRELIMINARY CALCULATIONS FOR 150AH,
30V BATTERY

Task I - B. 5. d. requires a preliminary design for a reserve battery capable of 80 amperes discharge for 1.875 hours (150Ah) at 28 + 2 volts. The discharge rate coincides closely with the 2.0A tests described in Section 2. 3. 3. 2, page 35. Therefore, Cell No. 7 from Table X, page 43, for which voltage time data are plotted in Figure 23, page 47, may be used as a basis for the necessary calculations.

Using the 35°C curve from Figure 23, nine cells would produce an initial closed circuit voltage of 3.25×9 , or 29.3V. At the cut-off voltage of 26V, the average cell potential is $26/9$, or 2.89V. To this cut-off point, Cell No. 7 delivered about 1.85 hours, or 3.70Ah.

In the present calculations, an individual cell capacity of 50Ah will be used. This is done to limit electrode area and cell volume to what appears practical from cell pressure and internal heating considerations. Therefore, to obtain the desired 150Ah capacity, three 9-cell units in parallel connection would be used.

Positive electrode area required for 50Ah capacity is 9 sq. in. for the 3.7Ah cell $\times 50/3.70$, or 121.5 sq. in. Assuming 3.25 x 3.75 in. electrodes, a cell having 10 positive and 11 negative plates has a positive and negative electrode area of 122 and 134.2 sq. in., respectively. The component weights for the 50Ah cell can then be calculated from the data for Cell N. 7 in Table X as follows:

Positive electrodes, less grids:

$$12.0\text{g in the 9 sq. in. cell} \times \frac{122}{9} = 162.5\text{g}$$

Negative electrodes, less grids:

$$0.040 \times 134.2 \times 16.4 \times 0.53 = 46.6\text{g}$$

$$\text{Electrolyte: } 18 \times \frac{122}{9} = 244.0\text{g}$$

Grids (including tabs):

$$0.21(122 + 134.2 + 31.5) = 60.4\text{g}$$

$$\text{Separators: } 0.05 \times 3.5 \times 4.0 \times 20 = 14.0\text{g}$$

$$\text{P. E. envelopes: (0.005 in. thick)} = 4.0\text{g}$$

TOTAL

531.5g/cell, or
1.17 lbs/cell.

The thickness of each cell pack would be

positives	10 x .06	=	0.60 in.
negatives	11 x .04	=	0.44 in.
separators	20 x .015	=	0.30 in.
P. E. envelopes		=	0.01 in.
			<hr/>
TOTAL			1.35 in.

For nine cells, a battery case about 12-1/2 x 4-1/2 x 3-3/4 in. would be required. Using 1/8 in. thick aluminum and allowing an additional 25% for connectors and reinforcement, the case weight would be about 3.5 lbs, and the total 150Ah battery weight would be 27 x 1.17 + 3 x 3.5, or about 42 lbs. At the average potential of 28V, the electrical output of the battery is 150 x 28, or 4200Wh, and the energy density obtained is in the order of 100 Wh/lb.

8. APPENDIX E - ANALYSES OF CUPRIC FLUORIDE FROM OZARK-MAHONING AND LEDOUX CO.

SPARK SOURCE MASS SPECTROMETRY, ppm					EMISSION MASS SPECTROSCOPY, ppm			
Element	Led. ¹	Led. ²	Led. ²	O-M. ²	Led. ¹	Led. ²	Led. ²	O-M. ²
H	---	8.3	---	27	---	---	---	---
Li	<0.1	0.06	---	0.1	<1	---	---	---
Be	<0.3	4	---	---	---	---	---	---
B	<0.4	4	0.3	10.2	---	---	---	---
C	---	500	---	114	---	---	---	---
N	---	11	---	31	---	---	---	---
O	---	15000	---	1230	---	---	---	---
Na	3	48	1	204	2	8	---	---
Mg	9	---	4	42	---	3	2.7	35
Al	1.1	37	4	104	---	3	<5	170
Si	---	---	17	---	2	---	---	---
P	---	---	1.4	11	---	---	---	---
S	---	230	---	340	---	---	---	---
Cl	30	97	10	260	---	---	---	---
K	9	42	3	25	<10	---	---	---
Ca	---	10	5	21	---	5	6.9	86
Ti	<3	<10	---	<10	---	---	---	---
V	32	---	---	45	---	---	---	---
Cr	1	9.4	0.3	13	---	---	---	5
Mn	---	---	0.5	12	---	---	---	23
Fe	6	---	7	1200	5	5	<2	1100
Co	---	7.0	---	---	---	---	---	---
Ni	6	8.5	3	730	5	5	---	970
Zn	---	<10	---	250 ³	---	---	---	---
Ga	3	11	---	2.7	---	---	---	---
As	---	69	---	<11	---	---	---	---
Ag	---	---	---	26	---	---	---	6
Cd	---	---	---	70	---	---	---	---
Rb	---	5.0	---	---	---	---	---	---
Sn	---	---	---	4600	---	---	---	400
Te	---	<38	---	<38	---	---	---	---
Pb	---	---	30	270	---	---	---	120
Bi	---	---	---	300	---	---	---	---
Y	5	---	---	---	---	---	---	---

¹LEL, Lot 1 - Tested by Associated Electronic Labs.

²See NAS 3-8521, Final Report, R-7703.

³May be due to residuals in mass spectrometer.

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